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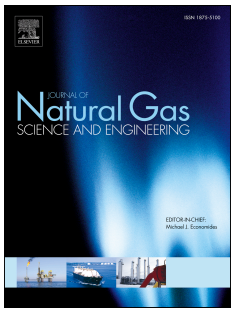

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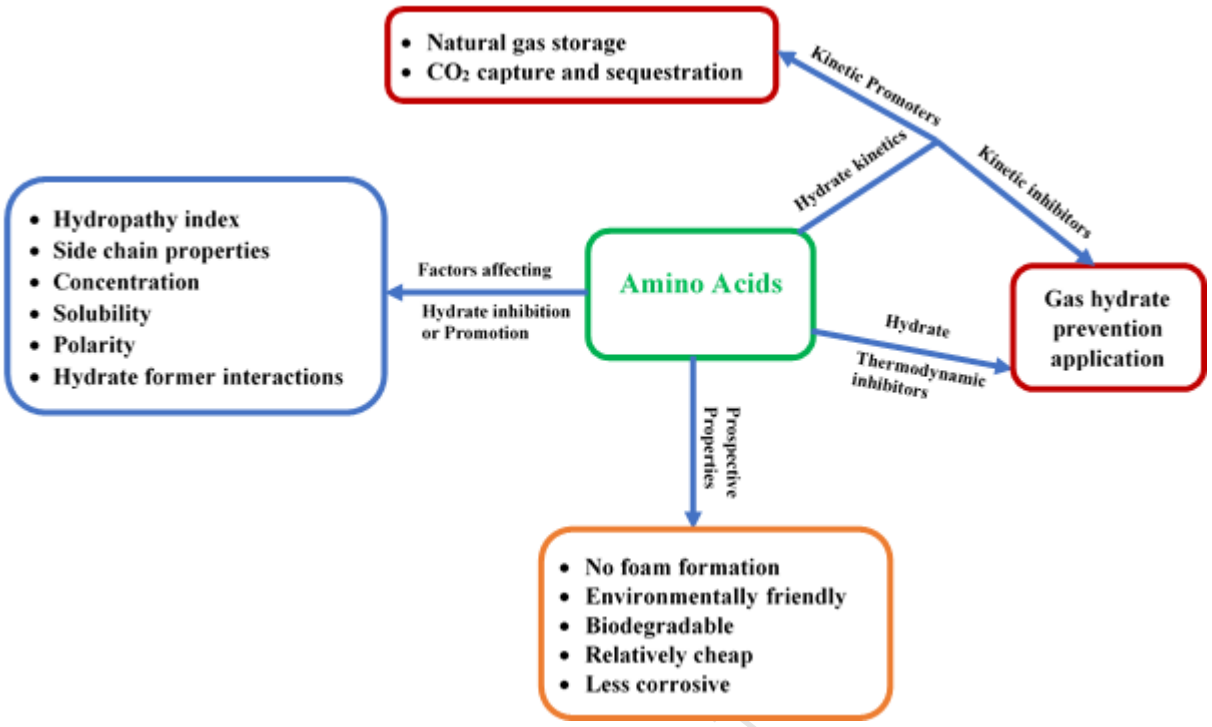

A Review on the Role of Amino Acids in Gas Hydrate Inhibition, CO_2 Capture and Sequestration, and Natural Gas Storage

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Abstract

Natural amino acids have been introduced as potential additives for gas hydrate inhibition, natural gas storage, and CO_2 capture and sequestration. Herein, almost all amino acids hydrate-based additives are critically reviewed. The hydrate inhibition/promotion effect of each amino acid and factors that affect their performance on gas hydrate formation are discussed. Furthermore, amino acids hydrate inhibition/promotional mechanism and modelling studies are reviewed. Detailed comparison between amino acids and convention hydrate additives alongside future directions towards amino acids hydrate-based technology commercialization are also discussed. The findings presented in this work are relevant for future amino acids breakthrough research in hydrate-based technologies.

Keywords: Gas hydrates; Amino acids; CO_2 capture; Natural gas storage; Thermodynamics; Kinetics

Contents

1. Introduction

Gas hydrates are ice-like crystalline compounds formed by the trapping of gas molecules in hydrogen bonded water molecules at high-pressure and low temperature conditions. The gas molecules are trapped in the water molecules through van der Waals forces (Koh et al., 2011; Sloan and Koh, 2007). Depending on the type, shape and size of the gas molecules, three basic gas hydrate structures occur: cubic structure I, cubic structure II and hexagonal structure H. Figure 1 shows the available gas hydrate structures (Sloan and Koh, 2007). Gas hydrate has applications such as future energy source (Englezos, 1993), CO_2 capture and gas separation (Babu et al., 2015; Park et al., 2013), storage and transportation of gases (such as natural gas, hydrogen, carbon dioxide and etc.) (Lang et al., 2010; Najibi et al., 2009; Strobel et al., 2006).

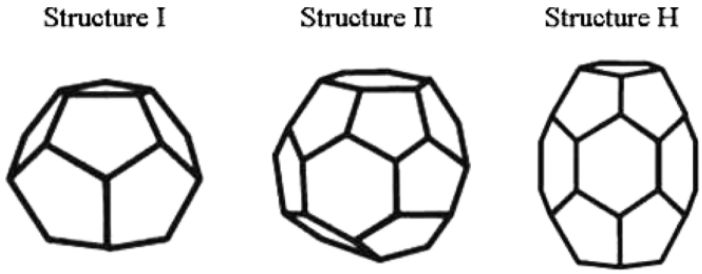

Figure 1. Common gas hydrate crystal structures (Tariq et al., 2014).

On the contrary, gas hydrate causes major flow assurance problems in the oil and gas industry. During hydrocarbons drilling, production and processing operations, gas hydrate forms in

pipelines and facilities which results in pipeline blockage, huge cost of prevention/removal, environmental hazards and sometimes loss of lives (Koh et al., 2011). Heating, water removal, depressurization and chemical injection are the techniques used to prevent or remove gas hydrate plugs in pipelines. However, chemical injection is widely used due to economic and current technological feasibility (Koh et al., 2011; Tariq et al., 2014). Generally, depending on the area of application, two major types of gas hydrate chemical additives (inhibitors/ promoters) are usually used to influence the formation of gas hydrate thermodynamically, by changing the hydrate phase equilibrium boundary conditions, and/or kinetically, by enhancing/delaying the hydrate formation nucleation and crystal growth rate.

Thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs) are the available chemical inhibitors. THIs (Glycols and methanol) inhibit gas hydrates thermodynamically by reducing the activity of water in hydrate formation by the formation of hydrogen bonds with water molecules. Hence, they increase the non-hydrate formation region of the hydrate formation phase boundary by shifting the equilibrium hydrate formation curve to high pressures and/or low temperatures. The use of THIs require high concentration, which results in high operational cost. At high subcooling temperatures, over 40 wt% is required to guarantee inhibition in most cases. Also, they are highly volatile, and thus environmentally prohibited (Bavoh et al., 2018b; Broni-Bediako et al., 2017). Alternatively, LDHIs comprises of kinetic hydrate inhibitors (KHIs) and anti-agglomerates. KHIs are generally polymers (polyvinylpyrrolidone and poly-N-VinylCaprolactam), and they prevent the formation of gas hydrates by sticking on the hydrate crystals to prolong or delay hydrate nucleation time (induction time) and growth rate. KHIs are used at low concentrations (< 2 wt%), however, they are ineffective at high subcooling and shutdown conditions, hence, it's encouraging to introduce

new chemical inhibitors which are environmentally friendly, less expensive, and highly effective to combat the above mentioned problems (Carroll, 2014; Kamal et al., 2016).

The application of hydrate-based technology for carbon capture and sequestration (CCS) and natural gas storage involves the use of chemicals to enhance hydrate formation instead of hydrate prevention in the case of flow assurance systems. Gas hydrate-based CCS initially involves CO_2 separation process via formation of CO_2 hydrates in a CO_2 mixed gas system (e.g flue gas and natural gas). Since CO_2 is very prone to hydrate formation at low pressures, its able to form hydrates faster with high gas (CO_2) to hydrate conversion ratio than other gases. The residual gas can be transferred to a vessel as demonstrated in Figure 2. The rich CO_2 hydrates are then dissociated to remove the CO_2 for further sequestration process similar to hydrate based natural gas storage process. The separated CO_2 can then be sequestrated or stored in reservoirs in hydrate form. Also, the CO2 hydrates can be deposited as hydrate pellets on sea bed conditions as long as they are stable.

Thermodynamic hydrate promoters (THPs) and kinetic hydrate promoters (KHPs) are the available gas hydrate chemical promoters. THPs are basically used to shift the hydrate phase boundary conditions to higher temperatures and low-pressure regions. KHPs are also employed to increase the hydrate induction time, formation rate, and the gas/water uptake during hydrate formation.

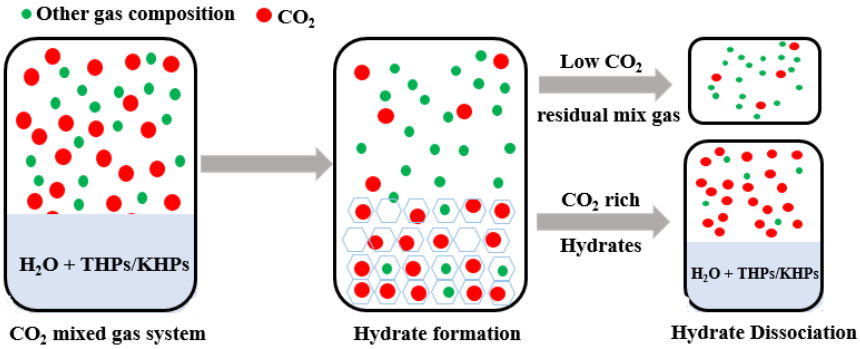

Figure 2. Hydrate-based gas separation process (CO_2 capture process) (Zheng et al., 2017)

Commonly used THPs are tetrahydrofuran (THF) (Rong et al., 2015) and acetone, while nano particles (Nashed et al., 2018b), Sodium dodecyl sulfate (SDS) (Pan et al., 2018; Zhiming Liu et al., 2018) and some other surfactants are KHPs. THPs and KHPs are applied in CO_2 capture and sequestration (Li et al., 2010; Park et al., 2013), and gas storage and transportation (Hao et al., 2008; Veluswamy et al., 2018). These conventional promoters just like conventional inhibitors are environmentally prohibitive and less effective.

Base on the general knowledge that compounds that exhibit strong electrostatic charges and/or strong hydrogen bond forming affinity can inhibit gas hydrates formation (Kim and Kang, 2011), some novel gas hydrate inhibitors have been introduced as potential inhibitors which may replace the commercially existing inhibitors. One of such classes of inhibitors are ionic liquids (Khan et al., 2017a, 2017b; Nashed et al., 2018a; Tariq et al., 2014; Xiao and Adidharma, 2009). Ionic liquids have attracted much attention due to their zero volatility and dual functionality in hydrate inhibition (Xiao and Adidharma, 2009) (i.e. they function as both THIs and KHIs). More details on ionic liquids (ILs) as gas hydrate inhibitors is presented in reference (Khan et al., 2019, 2018; Tariq et al., 2014; Yaqub et al., 2018). However, an IL review (Pham et al., 2010) shows that most commonly used ILs for gas hydrate inhibition are toxic in nature. In addition,

ILs are relativity expensive and might not be cost effective to be used in the oil and gas industry (Zare et al., 2013). This led to the introduction of amino acids as new gas hydrate inhibitors in 2011 by Sa et al., (2011). They reported that amino acids exhibit strong electric charges/electrostatic interactions with water as zwitterions and interact with water molecules through strong hydrogen bonding due to their hydrophilic nature which qualifies them as good inhibitors. This electrostatic interaction between amino acids and water molecules reduces the ice-like crystalline structure of the hydrogen bonded water molecules, thus, causing a negative affinity amongst them (Hecht et al., 1993; Nigam and Srihari, 2013; Pertsemlidis et al., 1996).

Generally, amino acids comprise of carboxylic acid, amine groups and a side chain (which ranges from apolar alkyl chain (hydrophobic) to a positive or negative charge moiety (hydrophilic)) with their chemical and physical properties strongly dependent on the particular side chain (Madeira et al., 2014; Vaitheeswaran and Thirumalai, 2008). Some key advantages of amino acids are their biologically friendly in nature and biodegradability. More so, amino acids are less expensive and can be purchased at relatively cheaper cost in bulk quantities. Amino acids are also reported (Badawy et al., 2005; Barouni et al., 2008) to act as corrosion inhibitors for metals in various chemical systems (such as sulphuric acid, aqueous chloride solutions in molar nitric mediums) which makes their use in the field application ease corrosion concerns. Based on these properties, amino acids have wide applications in areas such as biological science and biotechnology, pharmaceutical industry for protein purification (Arakawa et al., 2007). Most importantly, these properties make them potential candidates for gas hydrate inhibition in pipelines. In addition, not only has amino acids been reported as gas hydrate inhibitors, they are also reported as good gas hydrate promoter in both stirring and non-stirring condition, thus

making them good candidate for future gas hydrate-based applications in CO_2 capture, gas separation, storage and transportation.

The kinetics and thermodynamics data of gas hydrates in the presence of amino acids are critical for the developing effect of amino acids based hydrate inhibitors and promoters. Since gas hydrate-based research in the presence of amino acids (as gas hydrate inhibitors/promoters) is still at the early stages with several number of different studies been performed on its thermodynamics and kinetics, a critical review of the available data is therefore needed. Currently, no review article is reported in open literature on the use of amino acids as gas hydrate promoters/ inhibitors. Hence, a review of reported articles in open literature on gas hydrate-based applications using amino acids is presented herein. It will present up-to-date findings on amino acids as hydrate promoters and inhibitors and will be relevant for future potential research for the development and application of amino acids in hydrate based related technologies.

2. Role of amino acids in hydrate inhibition/CO_2 Capture/Natural gas storage

Review of literature shows that; thermodynamics and kinetics of gas hydrate studies have been studied in the presence of amino acids. However, most of the reported studies focused on the formation kinetics of gas hydrate which deals with CO_2 capture/separation and gas storage. The normal isochoric method with step heating is employed by researchers for thermodynamic studies while isothermal, constant cooling and isochoric method are employed for kinetic studies. For proper data analysis, data on amino acids as gas hydrate additives were gathered from open literature and analyzed separately for their thermodynamic effect and kinetic effect. All gas hydrate studied systems in the presence of amino acids with their respective tested concentrations and physicochemical properties are presented in Table 1.

156 Table 1. List of various studied amino acids + studied gas systems, concentrations used and physicochemical properties.

No	Amino Acid	Gas	Side chain Polarity	Side chain	Hydropathy index[d]	Test type	Conc.[a,b,c]	Remarks	Ref.
1	Glycine	CO_2	Nonpolar	-H	-0.4	THI	0.1[a] – 3.0[a]	Shows good thermodynamic hydrate inhibition impact.	(Sa et al., 2011)
2	L-Alanine	CO_2	Nonpolar	$-CH_3$	1.8	THI	0.1[a] – 2.2[a]	Thermodynamically inhibit CO_2 hydrates	
3	L-Valine	CO_2	Nonpolar	$-CH(CH_3)_2$	4.2	THI	0.1[a] – 0.5[a]	Shows thermodynamic CO_2 hydrate inhibition	
4	Glycine	CO_2	Nonpolar	-H	- 0.4	KHI	0.01[a] – 1.0[a]	Shows effective KHI impact by increasing the subcooling temperature and can eliminate the memory effect.	(Sa et al., 2013)
5	L-Alanine	CO_2	Nonpolar	$-CH_3$	1.8	KHI	0.1[a]	Demonstrates kinetic hydrate inhibition impact but less efficient than glycine.	
6	L-Valine	CO_2	Nonpolar	$-CH(CH_3)_2$	4.2	KHI	0.1[a]	Shows very less significant hydrate inhibition impact. Longer chins which are more hydrophobic do not inhibit hydrate. This is contrary to the understanding that hydrophobic compounds turns to be good KHIs (especially in ionic liquids (Tariq et al., 2014))	
7	Leucine	CO_2	nonpolar	$-CH_2CH(CH_3)$	3.8	KHI	0.1[a]	Shows very less significant hydrate inhibition impact.	
8	Isoleucine	CO_2	nonpolar	$-CH(CH_3)C_2H_5$	4.5	KHI	0.1[a]	Shows very less significant hydrate inhibition impact.	
9	Glycine	CO_2	nonpolar	-H	-0.4	Crystal structure	0.1[a] – 0.5[a]	Amino acids inclusion expands the hydrate crystal lattice, causing hydrate inhibition effect. At 2.2 mol% glycine's lattice expansion ability saturation is reached.	(Sa et al., 2014)
10	L-Alanine	CO_2	nonpolar	$-CH_3$	1.8	Crystal structure	0.1[a] – 0.5[a]	A structure I hydrate was formed with hydrate inhibition crystallization phenomenon. The lattice expansion magnitude was saturated at 0.5 mol%	
11	L-Valine	CO_2	nonpolar	$-CH(CH_3)_2$	4.2	Crystal structure	0.1[a] – 0.5[a]	All amino acids have a distinct crystal structure. However, the inhibition strength of amino acids depends on whether they act individually or agglomerate during hydrate crystallization.	
12	L-Alanine	CO_2	nonpolar	$-CH_3$	1.8	KHI + spectroscopy	0.01[a] – 0.1[a]	Delays hydrate nucleation and growth rate via disruption of the water structure in hydrate formation.	(Sa et al., 2015)
13	Aspartic acid	CO_2	acidic polar	$-CH_2COOH$	− 3.5	KHI + spectroscopy	0.01[a]	Delays hydrate nucleation and growth rate better than alanine but similar to asparagine via disruption of the water structure in hydrate formation.	

14	Asparagine	CO_2	polar	$-CH_2CONH_2$	− 3.5	KHI + spectroscopy	0.01[a]	Delays hydrate nucleation and growth rate via disruption of the water structure in hydrate formation.	
15	Phenylalanine	CO_2	nonpolar	$-CH_2C_6H_5$	2.8	KHI + spectroscopy	0.1[a]	Relatively shows no effect on the nucleation kinetics of hydrate formation, especially in memory water, due to its water structure hydrogen bonding strengthening ability. However, delays growth process but less than alanine.	
16	Histidine	CO_2	basic polar	$-CH_2C_3H_3N_2$	− 3.2	KHI + spectroscopy	0.1[a]	Efficient in hydrate inhibition than alanine but less than aspartic acid and asparagine via disruption of the water structure in hydrate formation.	
17	Glycine	C_2H_6	nonpolar	-H	- 0.4	KHI	0.05[b] – 3[b]	Shows strong KHI strength due to its lower hydrophobicity	(Rad et al., 2015)
18	Leucine	C_2H_6	nonpolar	$-CH_2CH(CH_3)$	3.8	KHI	0.05[b] – 3[b]	Inhibits hydrate formation kinetics but less than glycine.	
19	Asparagine	CH_4	polar	$-CH_2CONH_2$	− 3.5	KHI + MD simulation		Efficiently suppress hydrate formation kinetics. Asparagine do not adsorb on the gas/water interface during hydrate inhibition.	(Oluwunmi et al., 2015)
20	Glycine	THF	nonpolar	-H	- 0.4	KHI	0.05[b] - 1.5[b]	Shows strong KHI strength due to its lower hydrophobicity	(Naeiji et al., 2014a)
21	Leucine	THF	nonpolar	$-CH_2CH(CH_3)$	3.8	KHI	0.05[b] - 1.5[b]	Inhibits hydrate formation kinetics but less than glycine.	
22	L-threonine	CH_4	polar	$-CH(OH)CH_3$	− 0 .7	KHI	2770[c] - 1385[c]	Shows no significant KHI effect in delaying hydrate nucleation in both fresh and memory system.	(Perfeldt et al., 2014)
23	L-valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	KHI	2770[c] - 1385[c]	Shows no significant KHI effect in delaying hydrate nucleation in both fresh and memory system.	
24	L-histidine	CH_4	Basic polar	-NH-CH=N-CH=C-CH2	-3.2	KHI	0.1[b] – 1[b]	Significantly promotes hydrate formation than SDS.	(Bhattacharjee et al., 2016)
25	PVP and L-Tyrosine	NG	Polar	$-HO-Ph-CH_2$	-1.3	KHI	1[b]	The presence of tyrosine improves the hydrate inhibition impact of NaCl + PVP system.	(Kakati et al., 2016a)
26	PVP and L-Tyrosine	NG	Polar	$-HO-Ph-CH_2$	-1.3	KHI	100[c] – 275[c]	Tyrosine is a strong inhibitor than PVP and its addition into PVP enhances hydrate nucleation time in several folds.	(Talaghat, 2014)
27	Glycine	CH_4	nonpolar	-H	-0.4	THI	0.5[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	(Sa et al., 2016)
28	Alanine	CH_4	nonpolar	$-CH_3$	1.8	THI	0.5[a] – 2.2[a]	Inhibits hydrate phase boundary curve with concentration.	
29	Serine	CH_4	polar	$-HO-CH_2$	-0.8	THI	1.3[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	
30	Proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	THI	1.3[a] – 9[a]	Inhibits hydrate phase boundary curve with concentration.	

31	Glycine	CH_4	nonpolar	-H	-0.4	KHI	0.1[a]	Exhibits hydrate nucleation time and growth rate delay in both fresh and memory water	
32	Alanine	CH_4	nonpolar	$-CH_3$	1.8	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
33	Serine	CH_4	polar	$-HO-CH_2$	-0.8	KHI	0.1[a]	Exhibits hydrate nucleation time and growth rate delay in both fresh and memory water	
34	Proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
35	Glycine	NG	nonpolar	-H	-0.4	THI	0.5[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	
36	Alanine	NG	nonpolar	$-CH_3$	1.8	THI	0.5[a] – 2.2[a]	Inhibits hydrate phase boundary curve with concentration.	
37	Serine	NG	polar	$-HO-CH_2$	-0.8	THI	1.3[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	
38	Proline	NG	nonpolar	$-NH-(CH_2)_3$	-1.6	THI	1.3[a] – 9[a]	Inhibits hydrate phase boundary curve with concentration.	
39	Glycine	NG	nonpolar	-H	-0.4	KHI	0.1[a]	Exhibits hydrate nucleation time and growth rate inhibition effect.	
40	Alanine	NG	nonpolar	$-CH_3$	1.8	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
41	Serine	NG	polar	$-HO-CH_2$	-0.8	KHI	0.1[a]	Could inhibit hydrate formation kinetics better than glycine	
42	Proline	NG	nonpolar	$-NH-(CH_2)_3$	-1.6	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
43	Glycine	CO_2	nonpolar	-H	-0.4	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate with increasing concentration	(Roosta et al., 2016)
44	Proline	CO_2	nonpolar	$-NH-(CH_2)_3$	-1.6	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate with inhibition strength less than glycine but similar with serine and threonine.	
45	Serine	CO_2	polar	$-HO-CH_2$	-0.8	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate	
46	Threonine	CO_2	polar	CH_3-CH(OH)	-0.7	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate	
47	Glutamine	CO_2	polar	$H_2N-CO-(CH_2)_2$	-3.5	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate with the least inhibition strength compared with other studied amino acids.	
48	Histidine	CO_2	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI	0.5[b] – 2[b]	Shows the highest hydrate formation inhibition impact compared with other studies amino acids.	
49	Glycine	CH_4	nonpolar	-H	-0.4	THI	5[b] – 20[b]	Shows the highest hydrate phase behavior conditions inhibition compared with other studied amino acids.	(Bavoh et al., 2016b)
50	Alanine	CH_4	nonpolar	$-CH_3$	1.8	THI	10[b]	Inhibits gas hydrate thermodynamically.	

51	Serine	CH_4	polar	-HO-CH_2	-0.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
52	Proline	CH_4	nonpolar	-NH-$(CH_2)_3$	-1.6	THI	10^b	Inhibits gas hydrate thermodynamically.	
53	Arginine	CH_4	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	THI	10^b	Inhibits gas hydrate thermodynamically.	
54	Glycine	CO_2	nonpolar	-H	-0.4	THI	5^b – 20^b	Shows the highest hydrate phase behavior conditions inhibition compared with other studied amino acids.	(Bavoh et al., 2017)
55	Alanine	CO_2	nonpolar	-CH_3	1.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
56	Serine	CO_2	polar	-HO-CH_2	-0.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
57	Proline	CO_2	nonpolar	-NH-$(CH_2)_3$	-1.6	THI	10^b	Inhibits gas hydrate thermodynamically.	
58	Arginine	CO_2	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	THI	10^b	Inhibits gas hydrate thermodynamically.	
59	L-Leucine	CH_4	nonpolar	-$CH_2CH(CH_3)$	3.8	KHP/morphology	0.1^b – 0.5^b	Shows kinetic promotion with no promotion effect observed below 0.3 wt%.	(Veluswamy et al., 2016)
60	L- Methionine	CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP	0.02^b – 1^b	Significantly promotes hydrate formation uptake without the use of energy-intensive mixing.	(Cai et al., 2017)
61	L-norvaline	CO_2	nonpolar	C10H19NO4	-	KHP	0.02^b – 1^b	Promotes hydrate formation with similar promotion impact as L-norleucine	
62	L-norleucine	CO_2	nonpolar	C6H13NO2	-	KHP	0.02^b – 1^b	Promotes hydrate formation	
63	2-aminoheptanoic acid	CO_2	acid	C7H15NO2	-	KHP	0.02^b – 1^b	Promotes hydrate formation but with less promotion impact compared with L-norleucine	
64	n-hexanoic acid	CO_2	acid	CH 3 4COOH	-	KHP	0.02^b – 1^b	Promotes hydrate formation with similar promotion impact as 2-aminoheptanoic acid	
65	n-hexylamine	CO_2	nonpolar	CH3CH2CH2CH 2CH2CH2NH2	-	KHP	0.02^b – 1^b	Promotes hydrate formation	
66	L-tryptophan	CH_4	nonpolar	Ph-NH-CH=C-CH2-	-0.9	KHP	0.01^b – 0.3^b	Shows good kinetic hydrate formation enhancement effect in both stirred and unstirred systems.	(Veluswamy et al., 2017)
67	L-histidine	CH_4	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHP	0.03^b – 1^b	Shows hydrate formation promotion effect similar to arginine but less than tryptophan. Higher hydrophobic amino acids show less hydrate promotion effect.	
68	L-arginine	CH_4	basic polar	HN=C(NH2)-NH-	-4.5	KHP	0.03^b – 1^b	Shows hydrate formation promotion effect	

				(CH2)3					
69	Lysine	CH_4	basic polar	H2N-(CH2)4-	-3.9	THI	5^b -10^b	Shows THI effect with increasing concentration.	(Mannar et al., 2017)
70	Lysine	CO_2	basic polar	H2N-(CH2)4-	-3.9	THI	5^b -10^b	Shows THI effect with increasing concentration.	
71	Arginine	CH_4	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	THI/KHP	1^b – 5^b	Slightly inhibits methane hydrate phase boundary as well as promoting hydrate formation uptake	(Bavoh et al., 2018c)
72	Valine	CH_4	nonpolar	-$CH(CH_3)_2$	4.2	THI/KHP	1^b – 5^b	Slightly inhibits methane hydrate phase boundary as well as promoting hydrate formation uptake. Shows high uptake than arginine.	
73	Valine,	CO_2	nonpolar	-$CH(CH_3)_2$	4.2	KHP	0.5^b	Promotes hydrate formation uptake about 1.2 times.	(Prasad and Kiran, 2018a)
74	Phenylalanine	CO_2	nonpolar	Ph-CH2-	2.8	KHP	0.5^b	Shows no significant hydrate promotion effect	
75	Cysteine	CO_2	nonpolar	HS-CH2-	2.5	KHP	0.5^b	Promotes hydrate formation uptake about 1.2 times.	
76	Methionine	CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP	0.5^b	Promotes hydrate formation uptake about 1.2 times.	
77	Threonine	CO_2	polar	CH_3-CH(OH)	-0.7	KHP	0.5^b	Shows no significant hydrate promotion effect	
78	Methionine	CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP/XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	(Prasad and Kiran, 2018)
79	Phenylalanine	CO_2	nonpolar	Ph-CH2-	2.8	KHP/ XRD	0.5^b	Shows less hydrate kinetics conversion rate, thus gives less hydrate formation uptake.	
80	Methionine	CH_4	nonpolar	CH3-S-(CH2)2-	1.9	KHP/XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
81	Phenylalanine	CH_4	nonpolar	Ph-CH2-	2.8	KHP/ XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
82	Methionine	CH_4 + CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP/XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
83	Phenylalanine	CH_4 + CO_2	nonpolar	Ph-CH2-	2.8	KHP/ XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
84	Glycine + ethylene glycol	CH_4	nonpolar	-H	-0.4	THI	1^b – 30^b 1:1 mixtures	Glycine can enhance the thermodynamic inhibition strength of ethylene glycol, shows strong synergic inhibition effect.	(Long et al., 2018)
85	Glycine	CH_4	nonpolar	-H	-0.4	MD simulation	0.45^b - 1.5^b	Shows hydrate kinetics inhibition effect but less than serine.	(Maddah et

86	Alanine	CH_4	nonpolar	$-CH_3$	1.8	MD simulation	0.45^b - 1.5^b	Shows hydrate kinetics inhibition	al., 2018)
87	Serine	CH_4	polar	$-HO-CH_2$	-0.8	MD simulation	0.45^b - 1.5^b	Shows efficient hydrate kinetics inhibition via interruption of the hydrogen bond network of water.	
88	Proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	MD simulation	0.45^b - 1.5^b	Shows hydrate kinetics inhibition effect as alanine	
89	L-leucine	CH_4 and NG	nonpolar	$-CH_2CH(CH_3)$	3.8	KHP	0.1^b – 1^b	Very efficient in promoting hydrate formation kinetics than all studied amino acids at low concentrations for both structure I and structure II natural gas hydrates systems.	(Liu et al., 2015)
90	L-isoleucine	CH_4	nonpolar	$-CH(CH_3)C_2H_5$	4.5	KHP	0.5^b	Exhibits good hydrate promotion ability similar to phenylalanine.	
91	L-valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	KHP	0.5^b	Enhances hydrate formation kinetics.	
92	L-threonine	CH_4	polar	$CH_3-CH(OH)$	-0.7	KHP	0.5^b -10^b	Enhances hydrate formation with decreasing concentration.	
93	L-alanine	CH_4	nonpolar	$-CH_3$	1.8	KHP	0.5^b -2^b	Exhibits negligible hydrate promotion effect with increasing concentration.	
94	L-proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	KHP	0.5^b	Exhibits less hydrate promotion effect.	
95	L-methionine	CH_4	nonpolar	$CH3-S-(CH2)_2-$	1.9	KHP	0.5^b	Shows good hydrate promoters strength.	
96	L-tryptophan	CH_4	nonpolar	$Ph-NH-CH=C-CH_2-$	-0.9	KHP	0.5^b	Shows good hydrate promoters strength.	
97	L-phenylalanine	CH_4	nonpolar	$Ph-CH_2-$	2.8	KHP	0.5^b	Shows good hydrate promoters strength.	
98	L-arginine	CH_4	basic polar	$HN=C(NH_2)-NH-(CH2)_3$	-4.5	KHP	0.5^b	Able to promote hydrate formation kinetics with decreasing stability.	
99	L-glutamic acid	CH_4	acidic polar	$HOOC-(CH_2)_2-$	−3.5	KHP	0.5^b	Able to promote hydrate formation kinetics with decreasing stability.	
100	L-histidine	CH_4	basic polar	$NH-CH=N-CH=C-CH_2$	-3.2	KHP	0.5^b	Able to promote hydrate formation kinetics with decreasing stability.	
101	L-serine	CH_4	polar	$-HO-CH_2$	-0.8	KHP	0.5^b	Exhibits less hydrate promotion effect	
102	L-aspartic acid	CH_4	acidic polar	$-CH_2COOH$	− 3.5	KHP	0.5^b	Exhibits less hydrate promotion effect	
103	L-valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	THI	1^b – 5^b	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	(Bavoh et al., 2018a)
104	L-threonine	CH_4	polar	$CH_3-CH(OH)$	-0.7	THI	1^b – 5^b	Shows less thermodynamic hydrate inhibition, however may	

								increase with concentration depending on its solubility.	
105	Asparagine	CH_4	polar	$-CH_2CONH_2$	− 3.5	THI	$1^b – 5^b$	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	
106	L-phenylalanine	CH_4	nonpolar	Ph-CH_2-	2.8	THI	$1^b – 5^b$	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	
107	Glycine	C_2H_6	nonpolar	-H	-0.4	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
108	L-serine	C_2H_6	polar	-HO-CH_2	-0.8	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
109	L-histidine	C_2H_6	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
110	Glutamine	C_2H_6	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI/KPI	$0.5^b – 1.5^b$	Exhibit promotion effect	
111	Glycine	CH_4 + C_3H_8	nonpolar	-H	-0.4	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect and enhances the inhibition effect of PVP more than serine	
112	L-serine	CH_4 + C_3H_8	polar	-HO-CH_2	-0.8	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect but slightly enhances PVP hydrate inhibition impact.	
113	L-histidine	CH_4 + C_3H_8	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	(Roosta et al., 2018)
114	Glutamine	CH_4 + C_3H_8	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI/KPI	$0.5^b – 1.5^b$	Exhibit promotion effect	
115	Glycine	CH_4 + THF	nonpolar	-H	-0.4	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
116	L-serine	CH_4 + THF	polar	-HO-CH_2	-0.8	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
117	L-histidine	CH_4 + THF	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI/KPI	$0.5^b – 1.5^b$	Exhibit weak hydrate inhibition effect	
118	Glutamine	CH_4 + THF	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI/KPI	$0.5^b – 1.5^b$	No significant effect	
119	Glycine	CH_4	nonpolar	-H	-0.4	KHI	$1^b – 7^b$	Poor kinetic hydrate inhibitor on the bases of induction time and hydrate formation onset temperature even at high concentrations.	(Xu et al., 2017)
120	PVCap + Glycine	CH_4 + THF	nonpolar	-H	-0.4	KHI	$1^b : 1^b – 5^b$	Efficiently improves PVCap hydrate inhibition strength to about 16 time.	

121	Glycine	CH_4	nonpolar	-H	-0.4	KHDP	0.01^b – 5^b	Efficiently enhances methane hydrate dissociation kinetics.	(Kumar et al., 2017)
122	L-serine	CH_4	polar	-HO-CH_2	-0.8	KHDP	0.01^b – 5^b	Enhances methane hydrate dissociation kinetics.	
123	L-histidine	CH_4	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHDP	0.01^b – 5^b	Efficiently enhances methane hydrate dissociation kinetics, with high methane recovery potential.	
124	L-threonine	CH_4	polar	CH_3-CH(OH)	-0.7	KHDP	0.01^b – 5^b	Enhances methane hydrate dissociation kinetics.	
125	L-tryptophan	CH_4	nonpolar	Ph-NH-CH=C-CH_2-	-0.9	KHDP	0.01^b – 5^b	Enhances methane hydrate dissociation kinetics.	
126	L-threonine	CH_4	polar	CH_3-CH(OH)	-0.7	KHDP	0.01^b – 5^b	Enhances methane hydrate dissociation kinetics.	
127	Proline	CH_4	nonpolar	-NH-$(CH_2)_3$	-1.6	KHDP	0.01^b – 5^b	Poorly enhances methane hydrate dissociation kinetics.	
128	Glycine + 1-Ethyl-3-methy-limidazolium chloride	CH_4	nonpolar	-H	-0.4	THI	5^b + 5^b	Glycine + 1-Ethyl-3-methy-limidazolium chloride has negligible effect on their pure system phase boundary. However, they inhibit methane hydrate formation.	(Bavoh et al., 2018c)

[a] mol%; [b] wt.%; [c] ppm; [d]extracted from reference (Kyte and Doolittle, 1982);
THI refers to Thermodynamic hydrate inhibitor; THP refers to Thermodynamic hydrate promoter; KHI refers to Kinetic hydrate inhibitor; KHP refers to Kinetic hydrate promoter; KHDP refers to Kinetic hydrate dissociation promoter.

157 *2.1. Role of amino acids in hydrate thermodynamics (phase behaviour)*

158 *2.1.1 Amino acids as thermodynamic inhibitors*

159 Generally, the Hydrate – Liquid –Vapor Equilibrium (HL_wVE) curve is determined by authors to
160 evaluate the thermodynamic effect of amino acids as gas hydrate inhibitors/promoters. Seven
161 amino acids (proline, glycine, alanine, arginine, serine and valine, lysine) have been studied as
162 THIs for CO_2, CH_4, and NG (CH_4 – 93.0%, C_2H_6 – 5.0%, C_3H_8 – 2.0%) (Bavoh et al., 2018b;
163 Bavoh et al., 2017, 2016b; Mannar et al., 2017; Sa et al., 2016, 2011) as shown in Table 2 The
164 experimental details of all reported measured HL_wVE data in amino acids are presented in Table
165 2.

166 Table 2. Amino acids HL_wVE data

Author	Amino acid	Gas	Conc./ mol%	T/K	P/MPa	Data points
Sa *et al*., 2011 (Sa et al., 2011)	Glycine	CO_2	0.1	274.55 -281.35	1.49-3.51	5
		CO_2	0.5	274.35-281.05	1.49-3.50	5
		CO_2	1.3	273.85-280.65	1.49-3.51	5
		CO_2	2.2	273.35-280.15	1.44-3.48	5
		CO_2	3	273.05-279.45	1.47-3.47	5
	Alanine	CO_2	0.1	274.55-281.45	1.49-3.52	5
		CO_2	0.5	274.25-280.95	1.48-3.49	5
		CO_2	1.3	273.75-280.35	1.47-3.49	5
		CO_2	2.2	273.25-279.95	1.46-3.48	5
	Valine	CO_2	0.1	274.45-281.35	1.48-3.51	5
		CO_2	0.5	274.15-280.85	1.48-3.50	5
Sa *et al*., 2016 (Sa et al., 2016)	Glycine	CH_4	0.5	274.45-284.85	2.940-8.965	5
		CH_4	1.3	273.95-284.30	2.953-8.93	5
		CH_4	2.2	273.35-283.75	2.942-8.923	5
		CH_4	3	272.85-283.05	2.916-8.871	5
		NG	0.5	276.25-286.75	1.248-4.086	5
		NG	1.3	275.85-286.45	1.243-4.103	5
		NG	2.2	275.45-285.95	1.247-4.088	5
		NG	3	274.85-285.35	1.245-4.07	5
	Alanine	CH_4	0.5	274.25-284.85	2.947-8.952	5
		CH_4	1.3	273.95-284.15	2.953-8.928	5
		CH_4	2.2	273.05-283.58	2.932-8.914	5
		NG	0.5	276.15-286.65	1.251-4.102	5
		NG	1.3	275.75-286.35	1.245-4.106	5
		NG	2.2	285.75-275.15	1.237-4.086	5
	Serine	CH_4	1.3	273.75-284.05	2.938-8.94	5

		CH_4	3	272.65-282.85	2.937-8.889	5
		NG	1.3	274.85-285.45	1.241-4.066	5
		NG	3	273.65-283.75	1.234-4.055	5
	Proline	CH_4	1.3	283.85-273.65	8.934-2.941	5
		CH_4	3	272.3-282.50	2.929-8.868	5
		CH_4	6	268.40-278.65	28.87-8.698	5
		CH_4	9	264.90-274.00	2.839-8.473	5
		NG	1.3	274.85-285.45	1.241-4.066	5
		NG	3	273.65-283.75	1.234-4.055	5
		NG	6	270.75-280.65	1.235-3.995	5
		NG	9	267.65-276.75	1.206-3.932	5
Bavoh et al., (2016b)	Glycine	CH_4	5 wt%	277.90-285.20	4.550-9.840	4
		CH_4	10 wt%	277.25-284.50	4.650-9.980	4
		CH_4	15 wt%	276.80-283.73	4.600-9.650	4
		CH_4	20 wt%	276.50-283.10	4.800-9.770	4
	Alanine	CH_4	10 wt%	277.55-284.30	4.605-9.550	4
	Serine	CH_4	10 wt%	277.70-285.00	4.595-9.800	4
	Proline	CH_4	10 wt%	277.60-284.85	4.550-9.820	4
	Arginine	CH_4	10 wt%	278.55-285.40	4.700-9.650	4
Bavoh et al., (2017)	Glycine	CO_2	5 wt%	278.30-281.45	2.600-3.980	4
		CO_2	10 wt%	277.60-280.70	2.610-3.960	4
		CO_2	15 wt%	276.60-279.80	2.550-3.960	4
		CO_2	20 wt%	275.60-279.20	2.520-3.960	4
	Alanine	CO_2	10 wt%	277.60-280.87	2.560-4.000	4
	Serine	CO_2	10 wt%	278.20-281.30	2.600-4.000	4
	Proline	CO_2	10 wt%	277.70-281.10	2.530-4.020	4
	Arginine	CO_2	10 wt%	278.30-281.50	2.560-3.970	4
Mannar et al., (2017)	Lysine	CO_2	5 wt%	276.20-281.80	2.200- 4.010	4
		CO_2	10 wt%	276.45-281.03	2.000- 4.010	4
		CH_4	5 wt%	278.15-285.62	4.600-10.01	4
		CH_4	10 wt%	278.05-285.20	4.900-10.40	4
Bavoh et al., (2018b)	Arginine	CH_4	5 wt%	278.80-285.90	4.550-9.840	4
	Valine	CH_4	5 wt%	278.60-285.80	4.600-9.650	4
Long et al., (2018)	Glycine + ethylene glycol	CH_4	0.5 wt% + 0.5 wt%	279.70-287.80	5.050-12.20	5
	Glycine + ethylene glycol	CH_4	2.5 wt% + 2.5 wt%	279.10-286.70	5.110-11.98	5
	Glycine + ethylene glycol	CH_4	5 wt% + 5 wt%	277.10-285.40	4.780-11.47	5
	Glycine + ethylene glycol	CH_4	10 wt% + 10 wt%	274.70-282.20	4.880-11.47	5
	Glycine + ethylene glycol	CH_4	15 wt% + 15 wt%	273.30-279.90	4.810-11.15	5
Bavoh et al., (2018a)	Valine	CH_4	1 wt.%	276.20-284.10	3.600-8.10	4
			5 wt.%	275.70-283.50	3.500-8.00	4
	threonine	CH_4	1 wt.%	278.60-286.00	4.600-10.10	4
			5 wt.%	277.00-285.70	4.000-10.20	4

	Asparagine	CH_4	1 wt.%	277.90-286.10	4.300-10.30	4
			5 wt.%	275.80-283.70	3.500-8.10	4
	Phenylalanine	CH_4	1 wt.%	276.20-284.00	3.600-8.20	4
			5 wt.%	275.90-283.90	3.600-8.00	4
(Bavoh et al., 2018c)	Glycine + 1-Ethyl-3-methy-limidazolium chloride	CH_4	5 wt% + 5 wt%	277.80-284.90	4.700-9.99	4

Figures 3 and 4 illustrates the HL_wVE curve of CO_2, CH_4 and natural gas hydrates in the presents of amino acids at concentrations in mol % and wt %. In Figures 3 and 4, the addition of amino acids moves the HL_wVE curve to higher pressure and lower temperature regions. Thus, indicating a hydrate inhibition behavior by all studied amino acids in all studied gas systems. It's interesting to state that no THP effect has been reported on amino acids in open literature. The increasing order of inhibition for CO_2 hydrates is found to be valine > alanine > glycine as shown in Figure 3(a), a similar trend is observed for CH_4 and NG systems in Figure 3(b) and 1(c). However, a decreasing magnitude of inhibition of proline, followed by serine, alanine and glycine is observed based on mol %. However, an opposite inhibition strength of amino acids (glycine > alanine > proline > serine > arginine) is reported in Figure 4 for CH_4 hydrate based on wt %. The difference in inhibition trend is due to the choice of concentration units adapted by various researchers. The concentration units adapted for gas hydrate studies are very critical to evaluating and interpreting gas hydrate inhibition impact. Most reported amino acids thermodynamics hydrate based studies are measured in mol % (Sa et al., 2016, 2011). Figures 3 - 4, the equivalent concentration in mol % and wt % of amino acids, reveals significant difference in inhibition trend that may be capable of affecting their inhibition impact analyses using either concentration units. An opposing inhibition impact may be observed or reported considering both units, as suggested by Mech et al., (2015). For example, when mol % is used, amino acids

with heavy molecular weight (longer side chain) show high inhibition and vice versa. This can be well understood in Table 3. In Table 3, the equivalent wt.% concentration of the amino acids in mole % are low, with higher molecular weight amino acids have the lower mole% concentration values. Based on wt %, the hydrate inhibition impact increases as the molecular weight decreases (shorter side chain length) as shown in Figures 3 and 4. However, in most industrial applications wt % is used (Yousif, 1998). Therefore, for industrial focus research, using wt % might be appropriate as interpretation will contribute more towards practical field applications.

Based on wt %, glycine is the best amino acid THI. Long *et al*. (Long et al., 2018) found that, glycine is also able to improve the thermodynamic inhibition performance of ethylene glycol (a commercial THI) on CH_4 hydrates. They reported that 20 wt% glycine solution shows a methane hydrate phase boundary deviation temperature of 2.9 K (Bavoh et al., 2016b), while a combination of 10 wt% glycine and 10 wt% ethylene glycol shows 5.2 K (Long et al., 2018) as shown in Figure 5. Interestingly, the inhibition impact of 5 wt% glycine plus 5 wt% ethylene glycols and 10 wt% glycine is found to be in the same range in Figure 5. Thus, the thermodynamic inhibition enhancement of ethylene glycol by glycine is more evident at mixed concentrations above 5 wt%. However, synergy of glycine and 1- Ethyl-3-methy-limidazolium chloride (ionic liquid) at 10 wt.% (50/50) has negligible effect on the phase behavior of their pure compositions at the same concentration (Bavoh et al., 2018b). In addition, the inhibition effect of lysine was in the same range as alanine for methane and carbon dioxide at 10 wt% (Mannar et al., 2017). Meanwhile, valine shows very less methane hydrate and carbon dioxide hydrate inhibition, probably due to its longer alkyl side chain length (Bavoh et al., 2018c; Sa et al., 2011). The thermodynamic effect of threonine, valine, phenylalanine, and asparagine are not comparable to glycine and alanine at 5 wt.% for CH_4 hydrate formation (Bavoh et al., 2018a).

209 However, these amino acids are mostly methane hydrate kinetic promoters. For instance, in
210 carbon dioxide hydrate systems, asparagine and phenylalanine is known to act as promoters with
211 phenylalanine being able to promote CH_4 hydrate as well (Prasad and Kiran, 2018a; Sa et al.,
212 2015). Similarly, threonine and valine are able to promote CH_4 hydrates kinetically (Bavoh et al.,
213 2018b; Prasad and Kiran, 2018a, 2018b). The amino acids thermodynamic inhibition
214 mechanism is due to their electrostatic force of interactions via zwitterion interaction and
215 hydrogen bonding with water molecules. Thus, disturbing water role in hydrate formation and
216 resulting in hydrate inhibition (Bavoh et al., 2016b; Sa et al., 2015, 2011). An ANOVA analysis
217 at 95% confidence level indicted that, the amino acid thermodynamic inhibition impact is not
218 dependent on the type of guest compound (for only methane and carbon dioxide systems) and
219 that the thermodynamic inhibition impact of amino acids is solely due to its molecular
220 interactions with water molecules in the liquid phase. The amino acids gas hydrate phase
221 behavior inhibition strength is found to be influenced by their hydrophobicity, solubility in
222 water, side chain length, and concentration (Sa et al., 2011). However, all tested amino acids
223 inhibits hydrate with increasing concentration (Bavoh et al., 2016b; Sa et al., 2011).

224 Table 3. Variations in some studied amino acids concentration units

Wt.%	**Mol %**				
	Glycine	**Alanine**	**Proline**	**Serine**	**Valine**
5	1.25	1.05	0.82	0.89	0.80
10	2.60	2.20	1.71	1.87	1.68
15	4.06	3.45	2.69	2.94	2.64
20	5.66	4.81	3.76	4.11	3.70

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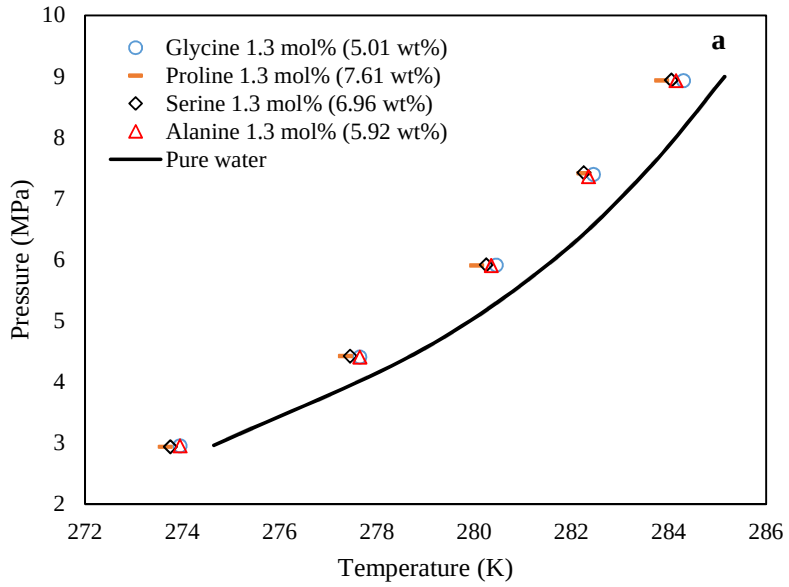
a
Glycine 1.3 mol% (5.01 wt%)
Proline 1.3 mol% (7.61 wt%)
Serine 1.3 mol% (6.96 wt%)
Alanine 1.3 mol% (5.92 wt%)
Pure water
Pressure (MPa)
Temperature (K)
10
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8
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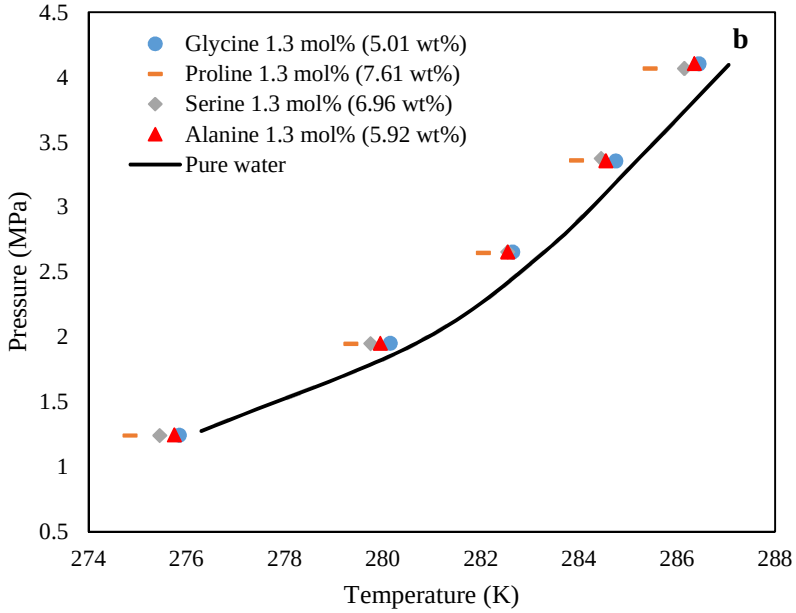
b
Glycine 1.3 mol% (5.01 wt%)
Proline 1.3 mol% (7.61 wt%)
Serine 1.3 mol% (6.96 wt%)
Alanine 1.3 mol% (5.92 wt%)
Pure water
Pressure (MPa)
Temperature (K)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
274
276
278
280
282
284
286
288

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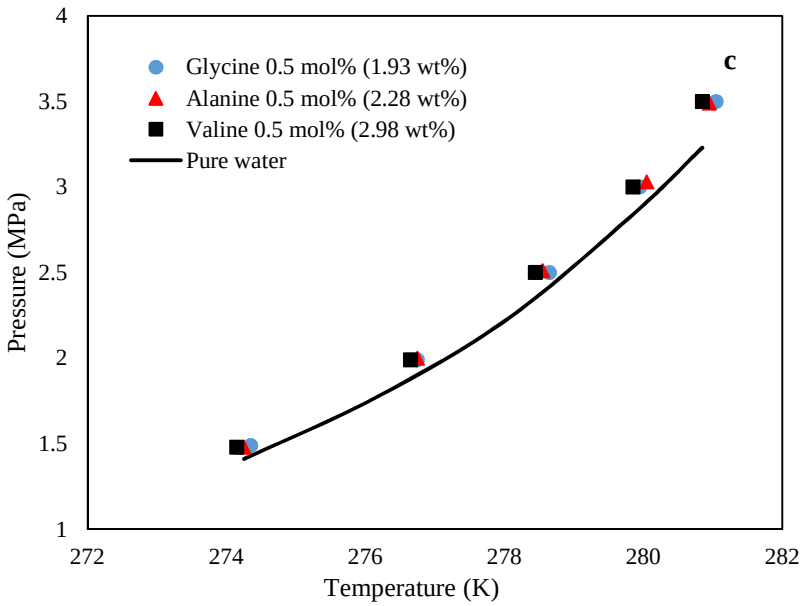


Figure 3. The inhibition strength of amino acids on the HL_wVE curve in various gas systems showing the effect of studied concentration units on inhibition impact. (a) CH_4 (Sa et al., 2016); (b) NG (Sa et al., 2016); and (c) CO_2 (Sa et al., 2011).

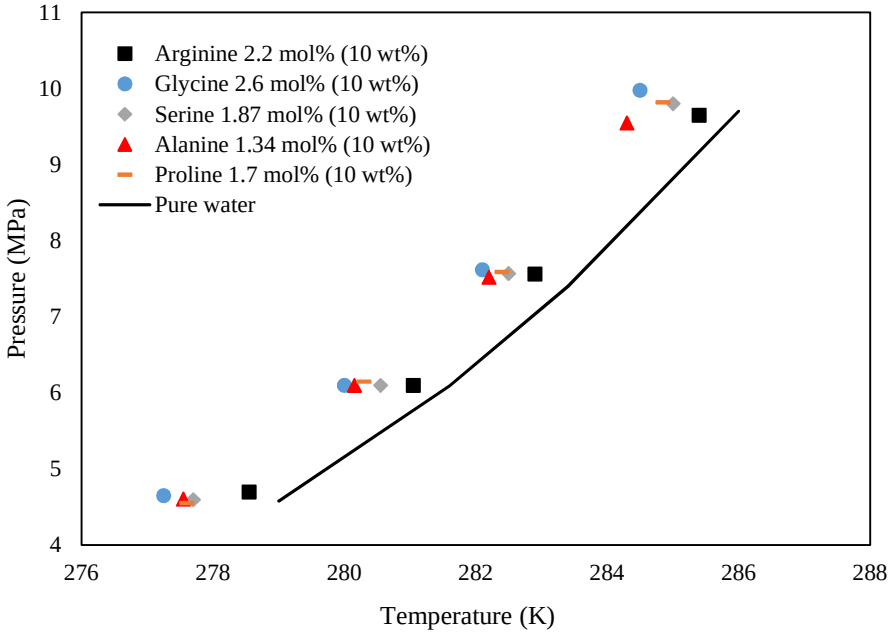


Figure 4. The inhibition impact of amino acids on the HL_wVE curve of CH_4 hydrate systems showing the effect of studied concentration units on inhibition impact (Bavoh et al., 2016b).

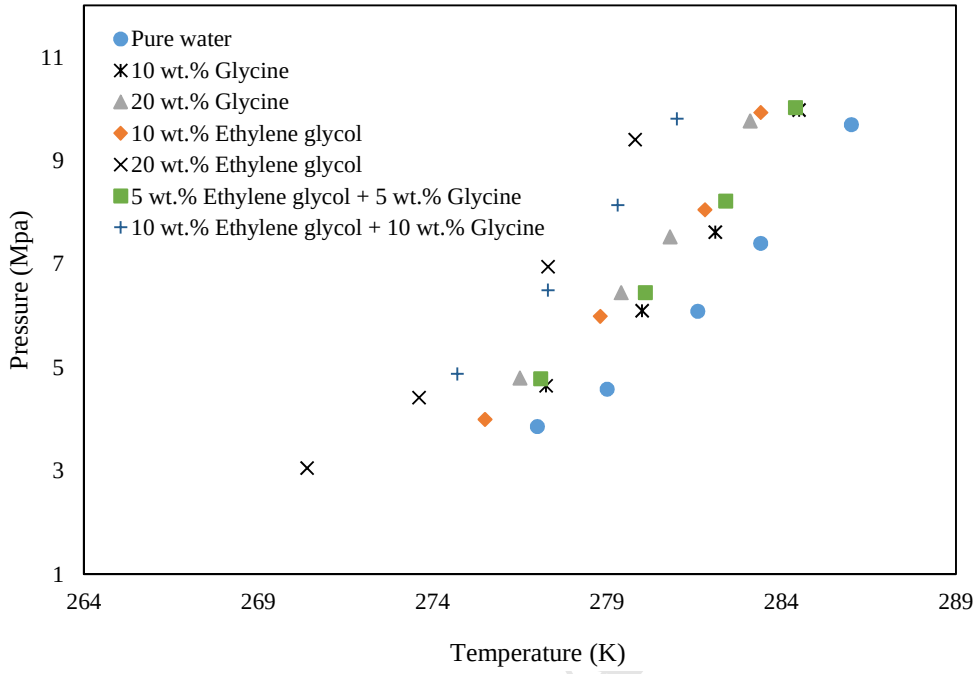


Figure 5. The inhibition impact of pure glycine and glycine + ethylene glycol on the HL_wVE data of CH_4 hydrates; Pure water and glycine data are taking from Bavoh et al., (2016b), glycol from Mohammadi and Richon, (2010), and glycine + ethylene glycol data from Long et al., (2018).

The affinity of each natural amino acid for water has been evaluated based on various physicochemical and interaction properties. These studies led to the development of amino acids side chain hydrophobic scale. There are several of such scales available (Dacheng et al., 1986; Zimmerman et al., 1968) as authors study different amino acid properties (e.g. surface tension, solubility, accessible surface areas, the energy of transfer of amino acids from water to a less polar environment, etc.) to propose/determine their hydrophobicity. Some authors (Naeiji et al., 2014b; Sa et al., 2015, 2011) have suggested that the inhibition effect of amino acids on gas hydrate is influenced by their hydropathy/hydrophobicity. The hydropathy of compounds has significant effect on their gas hydrate inhibition strength. This is well established in ionic liquids, as hydrate inhibition increases with decreasing hydropathy, which is related to the alky chain

length of compounds (Bavoh et al., 2016). Notwithstanding, with regards to amino acids, there are several amino acid hydropathy scales available in literature as summarized in Figure 6. However, a less agreement exists amongst all the hydropathy scales reported on amino acids as shown in Figure 6 which indicates that, amino acids hydropathy is less understood. Results in difficulties in the selection of a suitable hydropathy scale for gas hydrate data analysis and hence may possibly lead to the misinterpretation of results or errors in gas hydrate data analysis.

The hydropathy of a compound (amino acid) basically refers to hydrophilicity and hydrophobicity. This describes the ability of amino acids to have access to water molecules and or hinder their access to interact with water (Kyte and Doolittle, 1982). Amino acids hydropathy has been a difficult area of study as there are different hydropathy scales available in literature based on various properties such as solubility and surface tension etc. In these scales, numbers are assigned to each amino acid to describe its hydropathy strength. Higher hydropathy values represent strong hydrophobicity while lower values represent strong hydrophilicity.

Generally, gas hydrate researchers (Sa et al., 2015, 2011) adapt the amino acid hydropathy scales suggested by Kyte and Doolittle, (1982). Reasons for choosing these scales are not stated. Perhaps because it is the most widely used amino acid hydropathy scale in literature. Figure 7 shows the correlation between amino acids gas hydrate inhibition (average temperature depression) impact and their hydropathy scale proposed by Kyte and Doolittle, (1982). In Figure 7(a), an R^2 of 0.46 and 0.38 are observed for methane and natural gas hydrate inhibition respectively, while and R^2 of 0.67 is shown for methane in Figure 7(b). It can be observed that the strength of hydrate inhibition of amino acids does not strongly correlate with their respective hydropathy in Figure 7. Meanwhile, this hydropathy scale is generally the basis for analyzing hydrate inhibition impact in the presence of amino acids by researchers (Sa et al., 2011). Such

analysis is misleading and may result in data analytical errors, hence, we suggest further studies in selecting/developing a best amino acid hydropathy scale for hydrate inhibition purposes. It must be stated that, the R^2 values in Figure 7 may be affected by the number of data points employed for the correlation analysis, as limited data are currently available in open literature. Therefore, more experimental hydrate phase equilibrium data of amino acids are required to fully comprehend the effect of amino acid hydropathy on their inhibition impact. Compared to glycine, serine is less effective in preventing hydrate formation though it has very low hydropathy value (-0.8) compared to glycine (0.4). Hence, relying on only the hydropathy scale to justify the hydrate inhibition effect of amino acids is not sufficient. Other characteristics such as amino acids pH level (acidity), side chain polarity, and side chain group type (acyclic, aliphatic, aromatic, containing sulfur or hydroxyl etc.) should critically be considered when discussing the inhibition or promotion impact of amino acids on gas hydrate formation.

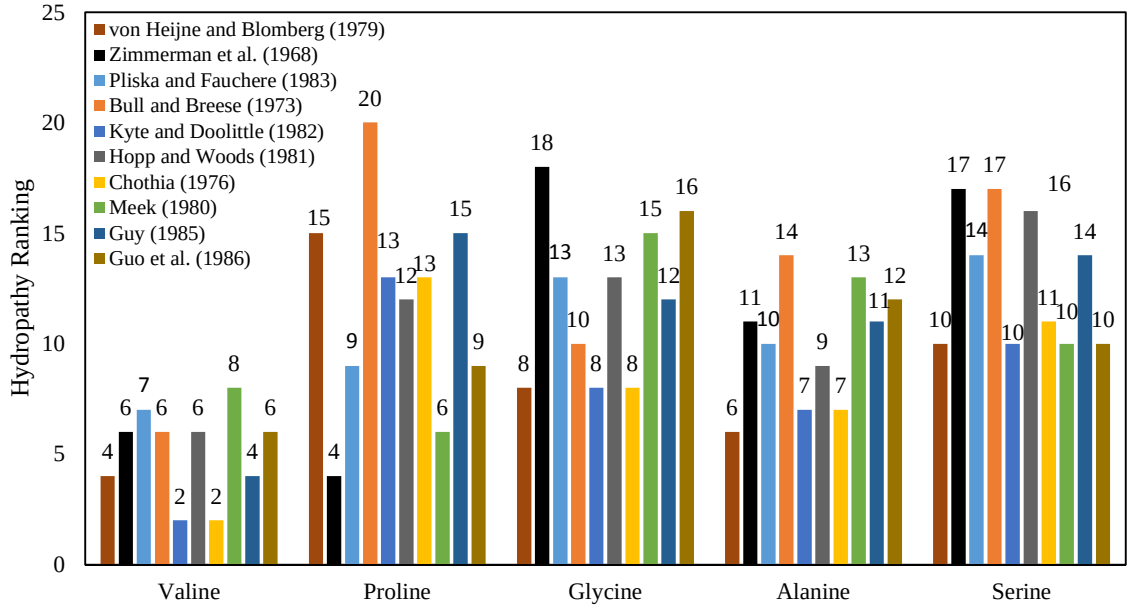
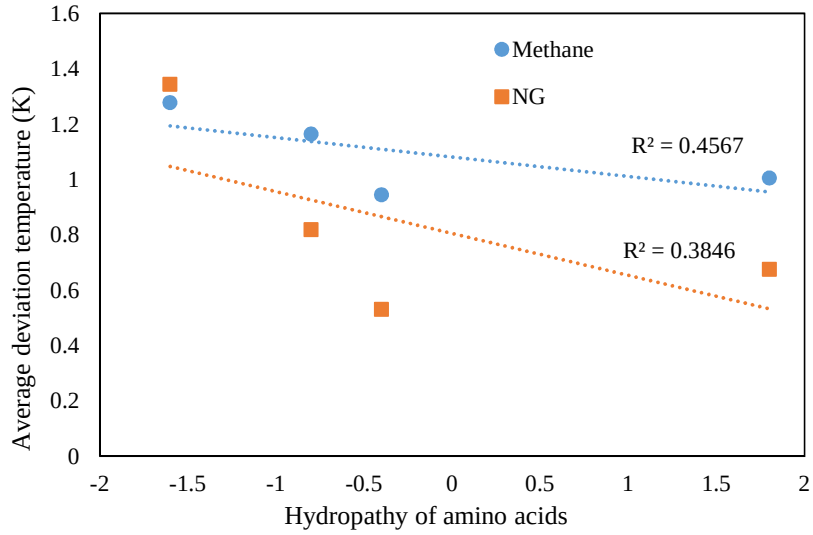


Figure 6. Hydropathy ranking of studied for gas hydrate inhibition. Data is taken from Wilce et al., (1995). The hydropathy of amino acids decreases with increasing ranking number.

290



(a)

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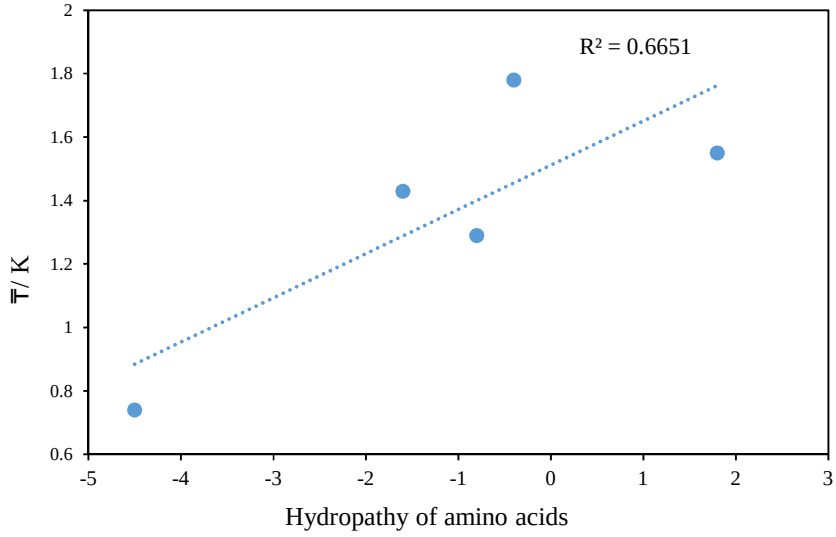

(b)

292

293 Figure 7. Regression between average depression temperature (Ŧ) and commonly used amino acid hydropathy scale
294 proposed by Kyte and Doolittle, (1982); (a) data from Sa et al., (2016) and (b) data from Bavoh et al., (2016b).

295

296 The solubility of THIs in water is critical in inhibiting gas hydrate. Conditions such as low
297 temperature during hydrate formation and acidic environment in the solutions caused by the
298 dissolved gases such as carbon dioxide decrease the solubility of the amino acids. Sa et al.,

(2011) determined the solubility of amino acid using the van'tHoff equation to account for amino acid solubility reduction due to the acidic environment. They suggested that, the amino acid solubility reduction due to acidic environment is negligible and therefore only the effect on decreasing temperature should be considered. Hence, the hydrate inhibitory efficiency of each amino acid increases with concentrations within their respective solubility in water.

2.2 Role of amino acids in hydrate kinetics

2.2.1 Amino acids as kinetic inhibitors

Unlike thermodynamic studies, relatively many studies are available on the kinetics of amino acid on gas hydrate mitigation/enhancement. The kinetic data gathered was considered differently since gas hydrate formation kinetics is very probabilistic, and dependent on factors such as apparatus design, experimental procedure, reactor wall roughness, driving force, and impurities in sample (Sloan and Koh, 2007). Generally, the three main kinetic indicators used to evaluate the inhibition/ promotion performance of amino acids are nucleation time, rate and gas uptake during hydrate formation. Mostly, nucleation time is preferred among the others as it characterizes the efficiency of amino acids in delaying hydrate formation. It must be stated that, on the bases of kinetic measurements, amino acids are very poor gas hydrate kinetic inhibitors. They are more kinetic promoters than inhibitors. However, their kinetic inhibition strength lies in their ability to delay the hydrate formation growth rate and gas uptake. The kinetic inhibition parameters usually determined by authors are induction time (Bhattacharjee et al., 2016; Kakati et al., 2016a; Naeiji et al., 2014a; Rad et al., 2015; Talaghat, 2014) and onset hydrate formation temperature (subcooling temperature) (Kakati et al., 2016a; Perfeldt et al., 2014; Sa et al., 2016). Also, gas uptake (Bhattacharjee et al., 2016; Kakati et al., 2016a; Roosta et al., 2016; Sa et al.,

2016, 2015, 2013) and hydrate rate of formation (Roosta et al., 2016) are determined. Sa et al., (2013) studied the effect of 5 amino acids (Alanine, glycine, leucine, valine, and isoleucine) on CO_2 hydrates at 0.1 mol% by determining their subcooling temperature and gas uptake for fresh and memory water systems. Their findings showed that, glycine best inhibited CO_2 hydrates then alanine, followed by valine, leucine and isoleucine. Furthermore, the inhibition effect of glycine increased with increasing concentration. Sa et al., (2015) further extended their study on the inhibition impact of amino acids on CO_2 hydrate formation growth and nucleation kinetics at 0.01 and 0.1 mol% using five electrically charged and/or hydrophilic side chains amino acids namely: alanine, asparagine, aspartic acid, histidine, and phenylalanine. Asparagine and aspartic acid efficiently inhibits hydrate than alanine based on gas uptake at 0.01 mol%, while at 0.1 mol%, histidine exhibits strong inhibition, with alanine and phenylalanine next to histidine. According to Sa et al., (2015), the hydrate nucleation and growth inhibition trends of these amino acids correlated with their hydropathy index showed similar trends at both low (0.01 mol%) and high (0.1 mol%) studied concentration. In addition, histidine performed better than alanine in delay hydrate nucleation time and growth. However, phenylalanine was less efficient in preventing hydrate formation compared with alanine. Phenylalanine virtual had no significant impact in delaying hydrate nucleation process. Interestingly, unlike glycine (in Sa et al., (2013) previous study), the inhibition impact of aspartic acid and asparagine decreased at increasing concentration due to their solubility limitations leading to residuals of excess (unreacted) amino acid in the system, which serves as site for enhancing hydrate formation. Hence, reducing their (aspartic acid and asparagine) kinetic inhibitory efficiency. Roosta et al., (2016) reported that, the kinetic inhibition effect of amino acids on CO_2 hydrates is due their side chain hydrophobicity and electrically charge. Thus, histidine showed high inhibition impact than

glycine, followed by proline, whose inhibition strength is in the same range with serine and threonine but higher than glutamine. It must be stated that, the correlation between the amino acids side chain properties and inhibition impact is not well understood and requires further studies. However, amino acids with polar side chains generally seem to show better CO_2 hydrate inhibition than non-polar ones.

Perfeldt et al., (2014) reported that valine exhibits slightly higher CH_4 hydrate inhibition than threonine. They could inhibit CH_4 hydrate than some anti-freeze proteins. However, a recent study has shown that glycine, serine, proline, and alanine could inhibit methane and natural gas (93% CH_4, 5% C_2H_6, 2% C_3H_8) hydrate at 0.1 mol% on the basis of onset temperature and gas uptake evaluation. Proline was the best among all the studied amino acids. Talaghat, (2014) suggested that, tyrosine could delay the induction time of NG hydrate better than PVP via a mini flow loop apparatus at 200 ppm. Furthermore, they augured that, the addition of tyrosine to PVP increased the inhibition impact of PVP. A study by Kakati et al., (2016a) reported that the incorporation of tyrosine synergically with PVP is able to boost the kinetic inhibition efficiency of PVP for NG hydrate system. Xu et al., (2017) argued via methane hydrate formation kinetics that, glycine poorly mitigates hydrate formation than PVCap. However, it can improve the efficiency of PVCap in many folds (of about 16 times). This demonstrates the ability of amino acids to inhibit gas hydrate and at the same time boost the performance of conventional kinetic inhibitors in the oil and gas industry. On contrary to the poor performance of amino acids in delaying hydrate nucleation time when applied in their pure state, they are able to increase the induction time of conventional kinetic inhibitors when mixed together. In the presence of THF and C_2H_6 hydrates, amino acid (glycine) is believed to act a strong kinetic hydrate inhibitor than

l-leucine (Naeiji et al., 2014a). Thus, glycine seems to stand tall among all the studied amino acids as the best kinetic inhibitor in different hydrate formers systems.

One the other hand, amino acids have been applied as gas hydrate dissociation promoter (inhibition) for methane hydrate production. Kumar et al., (2017) filed a patent on natural methane hydrate recovery via amino acids; glycine, histidine, proline, tyrosine, serine, threonine, and tryptophan. The patent claims, all tested amino acids efficiently promote methane hydrate dissociation kinetics after 18 minutes at 283 K in comparison with the base sample (pure water). However, in a stirred reactor, glycine and histidine show high hydrate dissociation enhancement impact. Histidine generally exhibits high methane recovery after 30 minutes with proline posing as the poorest in promoting methane hydrate dissociation. However, histidine could not beat the efficiency of ethylene glycol (a commercial hydrate thermodynamic inhibitor). This is because ethylene glycol effectively destabilizes hydrate phase better than histidine. In addition, the methane recovery further enhances with increasing additives (amino acids) injection rate (10 ml/ min and 30 ml/ min).

2.2.1.1 Amino acid kinetic inhibition mechanism

It's generally believed that commercially used gas hydrate kinetic inhibitors (polymers), inhibit hydrate by adsorption (Sloan and Koh, 2007). However a different inhibition mechanism is proposed by Sa et al., (2013) for amino acids by studying the effect of amino acid on CO_2 hydrate using synchrotron powder X-ray diffraction (PXRD) to identify the crystal structure of CO_2 hydrates and their lattice parameters. It was hypothesized that amino acids may have a hydrate growth inhibition mechanism different from that of PVP which is essentially driven by

388 adsorption. This growth inhibition mechanism is derived by perturbation of the local water
389 structure by amino acid hydrophilic terminal groups and the hydrophobic side chains via
390 hydrogen bonding as shown in Figure 8(a). Sa et al., (2015) further studied the perturbation
391 effect of amino acids on local water structure by obtaining the polarized Raman spectra of
392 aqueous amino acids solutions. Their findings revealed that amino acids perturbed the structure
393 of liquid water causing kinetic inhibition of gas hydrate formation nucleation and growth.
394 However, the intensity of perturbation depends on the amino acid side chain properties. Amino
395 acids with electrically charged and/or hydrophilic side chains were observed to disrupt the low
396 temperature liquid water structure, whereas those with hydrophobic side chains strengthened this
397 structure. Sa et al., (2014) studied crystallization phenomena of CO_2 hydrate in the presence of
398 amino acids using PXRD, 13 C cross-polarization (CP) nuclear magnetic resonance (NMR), and
399 Raman spectroscopy and results obtained was in contrary to the previously proposed gas hydrate
400 mitigation mechanism (perturbation of local water structure) in literature (Sa et al., 2015, 2013).
401 It was found that, amino acids form hydrogen bonds with water molecules, displacing the water
402 molecules in the hydrate crystal lattice, and incorporating themselves in the hydrate structure.
403 This incorporation of amino acids in hydrate lattice results in lattice distortion and expansion.
404 However, as the lattice sites for incorporation are saturated, those that are not incorporated into
405 the hydrate crystal lattice are excluded and crystallized among themselves. The excluded
406 crystallized amino acids may act as site for gas hydrate formation enhancement. It must be stated
407 that amino acid does not form semiclathrate hydrates, they only take part in lattice formation (see
408 Figure 8(b)). This has also been confirmed via estimation of the hydrate enthalpy of dissociation
409 using the Clausius-Clapeyron equation indicating that, amino acids do not participate in hydrate
410 cage occupation and structure during hydrate formation (Bavoh et al., 2017, 2016b). It must be

stated that Sa et al., (2015), (2014), (2013) findings requires more direct evidences and further molecular level confirmations to reveal amino acids hydrate inhibition mechanism. Since they basically relate the ice lattice Bragg peaks to sI hydrates, which may reflect the water to hydrates conversion rate in the system. Which could also be influence by the system driving force (especially at 3.6 MPa for CO_2 hydrates), stirring rate, gas to water ratio reactor design, etc. Moreover, the study on lattice incorporation by Sa et al., (2014) lacks quantitative analyses and provides limited crystalline information. It only provides profile refinement. Thus, a careful analysis of the lattice incorporation phenomena of amino acids in hydrate lattice structure is required because once it occurs, an adverse effect or change may happen in many lattice refinement parameters such as lattice parameter (a, b, c, <alpha>, <beta>, <gamma>), atomic site occupancies, atomic positions (x, y, z), profile parameters (U, V, W), etc which could change the structure. In addition, the idea of the incorporation of amino acids into hydrate lattices structures is expected to result in thermodynamic inhibition effect and not kinetic inhibition as suggested by Sa *et al* (Sa et al., 2014). This might be due to the perturbation kinetic inhibition mechanism discussed earlier in this section. Basically, the thermodynamic inhibition effect and the perturbation kinetic hydrate inhibition mechanism are all driven by the hydrogen bonding interaction between the hydrogen bonded water crystalline structure and the amino acids molecules. Hence, a large perturbation effect is caused with kinetically reduces the hydrate crystalline nucleation and growth rate.

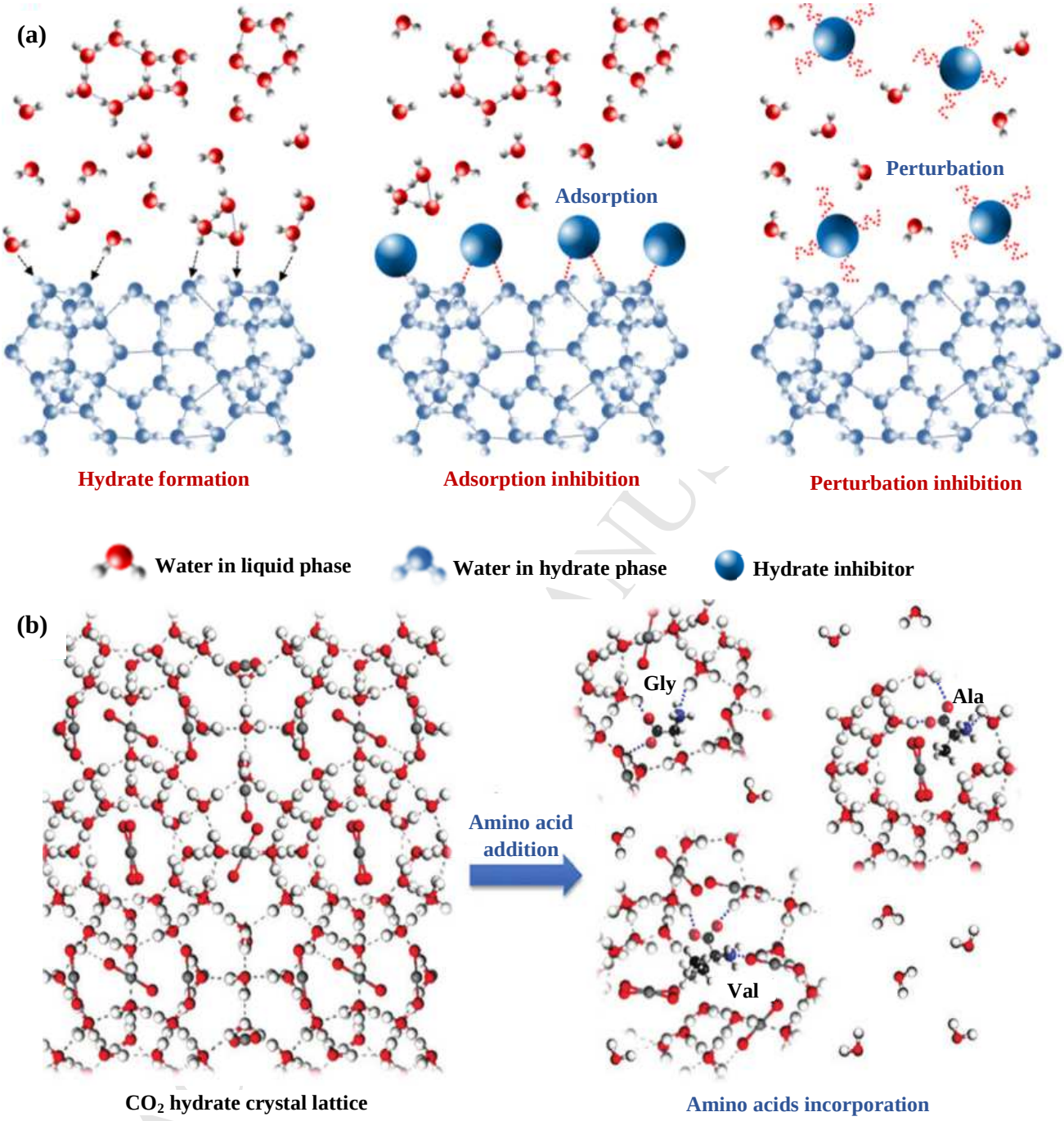

Figure 8. (a) amino acids gas hydrate growth inhibition mechanism by perturbation of the local water structure compared to adsorption inhibition mechanism (Sa et al., 2013); (b) amino acids lattice distortion and expansion inhibition mechanism through incorporation into gas hydrate crystal lattice (Sa et al., 2014). ©Nature Publishing Group. Reproduced by permission of Nature Publishing Group.

436 *2.2.2. Amino acids as kinetic promoters*

437 Gas hydrate promoters are additives that enhance hydrate formation. They either do so
438 thermodynamically or kinetically. Such additives are important for implementing gas hydrate-
439 based technologies such as natural gas storage and transportation, CO_2 capture, storage and
440 sequestration. One critical problem that limits the implementation of these technologies is how to
441 form hydrate very fast. The conventional gas hydrate promoters are THF (Sefidroodi et al., 2011;
442 Sowa et al., 2014; Strobel et al., 2006) and SDS (Kakati et al., 2016b; Partoon et al., 2013).
443 However, these promoters do not form hydrates so fast as may be required for their applications.
444 In addition, they are not environmentally friendly and their presence may result in foam
445 formation in process plants (Veluswamy et al., 2017). Recent, amino acids studies suggest that
446 amino acids are potential gas hydrate promoters. Most importantly the presence of amino acids
447 do not favour foam formation , thus can be applied in hydrate based commercial operations
448 (Veluswamy et al., 2017).

449 In this section, only kinetic amino acid based hydrate promoters are reported. Liu et al., (2015)
450 are among the first research group to report natural amino acids as methane hydrate promoters, at
451 low concentrations up to 1 wt%. According to the study, leucine showed the highest CH_4 hydrate
452 promotion effect than methionine, tryptophan, and phenylalanine, arginine, glutamic acid, and
453 histidine at 0.5 wt%. Leucine could convert about 95% water into methane hydrate with a
454 gravimetric capacity of 144 mgg^{-1} at an optimum concentration of 0.5 wt%. The presence of
455 leucine did not cause foaming upon degassing. However, l-serine, l-aspartic acid, and l-proline,
456 alanine show very less methane hydrate uptake (behaved as inhibitors as demonstrated by Sa et
457 al., (2016). Further details on the morphology changes of leucine during methane hydrate
458 formation and dissociation was studied by Veluswamy et al., (2016). However, no hydrate

459 enhancement effect was detected below 0.3 wt%. Veluswamy et al., (2017) further demonstrated
460 that, tryptophan could promote methane hydrate formation than histidine and arginine but could
461 not beat leucine. They argued that, the amino acid side chain properties play critical role in
462 hydrate promotion as amino acids with aromatic side chains that enhanced hydrate formation
463 better than those with aliphatic side chain. The combination of aromatic and hydrophobic side
464 chain could better promote hydrate formation. This may be true for methane hydrates, as the
465 amino acids promotion effect is composition dependent. All studied amino acids with aromatic
466 sided chain and hydrophobic nature (tryptophan, leucine, phenylalanine) have shown significant
467 methane hydrate promotion. However, leucine shows poor promotion effect (inhibition effect) in
468 ethane and THF hydrates (Naeiji et al., 2014a; Rad et al., 2015). Likewise phenylalanine is
469 reported to slightly inhibit CO_2 hydrates formation kinetics (Sa et al., 2015). In addition,
470 histidine is reported to show kinetic promotion effect on CH_4 hydrate (Bhattacharjee et al.,
471 2016). On the contrary, histidine is reported to kinetically inhibit CO_2 hydrates (Roosta et al.,
472 2016; Sa et al., 2015), indicating that, the kinetic promotion/inhibition effect of amino acids is
473 meaningfully dependent on the type of guest compound present. This composition dependent
474 hydrate promotion effect of amino acids provides selectivity opportunities for gas hydrate based
475 mixed gases separation and CO_2 capture applications. Interestingly, tryptophan and methionine
476 are able to promote both CH_4 and CO_2 hydrates (Cai et al., 2017). Other factors that contribute to
477 the promotion/inhibition effect of amino acids are their side chain length and hydropathy index.
478 Authors claim there is an optimum side chain length of hydrophobic amino acid in hydrate
479 kinetic promotion/inhibition (Cai et al., 2017; Sa et al., 2013). However, the optimum side chain
480 length is not clearly defined in current studies. According to Cai et al., (2017), L-methionine
481 could promote CO_2 hydrate formation better than L-norvaline, L-norleucine, 2-aminoheptanoic

482 acid, n-hexanoic acid, and n-hexylamine at 0.2 wt%. The gravimetric capacity of CO_2 hydrate
483 formation was about 356 mgg^{-1} in 1000 min for 81 mgg^{-1} bulk water system. It is worth noting
484 that, the promotion effect of amino acids is concentration dependent, which vary for every amino
485 acid in different gas system. For every gas system, all amino acids have an optimum
486 concentration above which their promotion/inhibition impact is decreased. For instant, the
487 optimum promotion impact of leucine in CH_4 hydrate is in the range of 0.3 – 0.5 wt% (Liu et al.,
488 2015; Veluswamy et al., 2016). In CH_4 hydrate system, the optimum concentration for
489 tryptophan is 0.3 wt%, while that for histidine and arginine is 1 wt% (Veluswamy et al., 2017).
490 In CO_2 hydrate L-methionine has an optimum concentration of 0.2 wt% (Cai et al., 2017). It is
491 recommended that authors optimize the effective promotion/inhibition concentration for amino
492 acids and compare them as such.

493 In Bhajan's lab, the effect of valine and arginine on CH_4 hydrates shows that, both valine and
494 arginine promote CH_4 hydrate formation more than SDS. Valine exhibits the most efficient
495 average methane hydrate promotion impact of about 10 and 1.3 times moles consumption of CH_4
496 than pure water and SDS. But the induction time for CH_4 hydrate nucleation was less compared
497 to SDS (Bavoh et al., 2018c). Prasad and Kiran, (2018a) also studied the effect of five amino
498 acids (L-valine, L-phenylalanine, L-cysteine, L-methionine and L-threonine) on CO_2 hydrate
499 formation under isochoric conditions in both stirring and non-stirring mode. They found that L-
500 valine, L-cysteine, and L-methionine increased the CO_2 uptake of water over about 20%, with
501 phenylalanine and threonine having negligible promotion or inhibition effect of CO_2 hydrate at
502 0.5 wt% in both stirring and non-stirring mode. Thus, showing that valine is able to promote both
503 CH_4 and CO_2 hydrate formation (Bavoh et al., 2018b; Prasad and Kiran, 2018a). A follow up
504 study with methionine and phenylalanine by Prasad and Kiran, (2018) on CH_4, CO_2 and their

505 mixture at 0.5 wt% using a non-stirred and isochoric mode reported that, the hydrate conversion
506 efficiency in phenylalanine is very low for CO_2 hydrate but both methionine and phenylalanine
507 show significant hydrate conversion efficiency in CH_4 and mixed CH_4 + CO_2 system. The
508 presence of methionine and phenylalanine enhanced the formation kinetics of hydrate formation
509 with about 90% gas to hydrate conversion and over 85% water to hydrate conversion within an
510 hour. Nonetheless, methionine promotes hydrate formation better than phenylalanine in both the
511 gas systems, but, phenylalanine is more recommended for methane hydrates only. The findings
512 further confirms that of Sa *et al.* (Sa et al., 2014) that amino acids form structure I hydrates. This
513 finding presents interesting bio potentials for the separation of CH_4 gas from CO_2+CH_4 gas
514 mixtures and natural gas storage.

515 *2.2.2.1 Amino acid kinetic promotion mechanism*

516 The amino acids hydrate promotion mechanism is controlled by lots of factors which are not
517 fully understood yet (Liu et al., 2015). The proposed amino acids hydrate promotion effect is
518 speculated by authors to arise from their surface activity and surface adsorption behavior via
519 capillary action (Cai et al., 2017; Liu et al., 2015; Veluswamy et al., 2017). The surface activity
520 of amino acids resulting in hydrate formation enhancement is similar to conventional surfactants.
521 Most amino acids molecular structure consist of both hydrophilic and hydrophobic nature arising
522 from the presence of amine and carboxylic acid groups and side chain. Furthermore, the amino
523 acids side chain may also vary based on its polarity, charge, and structure. This makes them
524 amphiphilic molecules; hence they can act as surfactants. (For example, leucine which is one of
525 the best reported amino acids promoter has a hydrophilic amine and carboxylic acid groups, and
526 a hydrophobic aliphatic isobutyl side chain). In addition, some amino acids (arginine and valine)
527 act as bio-surfactants and protein aggregation suppression (Tsutomu et al., 2007; Infante et al.,

528 2004, 1997; Pinazo et al., 2011). This surfactant behavior enables such amino acids to prevent/or
529 break the formation and agglomeration of hydrate nucleus crystals film at the gas/liquid
530 interface. Thus, allowing more gas to dissolve in the liquid phase for high hydrate gas uptake.
531 Linga's lab demonstrated that, hydrates formed in amino acids solution are very flexible and
532 porous in nature, which is responsible for their hydrate promotion effect (Veluswamy et al.,
533 2016). The presence of porous and flexible hydrates increases the surface adsorption ability at
534 the gas/liquid interface. This allows the sucking of more liquids to the gas/liquid interface via
535 improved capillary effect, resulting in high gas uptake into hydrate formation.

536 It is important to state that, amino acids promotion/inhibition mechanism in CO_2 systems is
537 partly influenced or controlled by the reaction between amino acids and CO_2 molecules. Details
538 on the reaction between amino acids and CO_2 is summarized by Zhang et al., (2018).
539 Zwitterionic reaction mechanism is mainly observed between amino acids and CO_2. In this
540 process, the amine group in the amino acids first reacts with the CO_2 to obtain intermediates as
541 zwitterions. The presence of any base (such as amine groups or water) in the system will result in
542 the formation of amino acids salts via reaction between the zwitterions and the base (Zhang et
543 al., 2018). Generally, the rate constant of the reaction describes the CO_2 adsorption rate, which is
544 related to the CO_2 hydrate formation rate and uptake. Thus, amino acids with fast rate of reaction
545 will potential promote hydrate formation and vice versa.

546 **3. Comparison of amino acids with other hydrate-based application additives**

547 In this section, the thermodynamic and kinetic inhibition/promotion effect of amino acids are
548 compared with commercially available inhibitors and promoters to evaluate their efficiency and

549 applicability in industrial operations. The discussion is divided into two sections;
550 Thermodynamics and kinetics. All hydrate phase behavior studies in amino acids have not shown
551 hydrate promotion effect. Hence, only THI effect is compared in this study. The THI effect of
552 the best performed amino acids is compared with commercially used inhibitors such as methanol
553 (Heng-Joo Ng, 1985; Mohammadi and Richon, 2010), ethanol (Maekawa, 2010; Mohammadi et
554 al., 2008a), ethylene glycol (Mohammadi and Richon, 2010)(Maekawa, 2010), diethylene glycol
555 (Maekawa, 2010), triethylene glycol (Maekawa, 2010; Sloan and Koh, 2007), and glycerol
556 (Breland and Englezos, 1996; Mohammadi et al., 2008b) for methane and carbon dioxide
557 hydrates at 10 wt.% as shown in Figure 9.

558 Methanol, ethanol and ethylene glycol are more efficient than amino acids (glycine and alanine)
559 as illustrated in Figure 9. However, amino acids are green compounds and are less expensive in
560 large quantities. On the other hand, amino acids are THIs than triethylene glycol but have similar
561 inhibition performance as glycerol and diethylene glycol in methane and carbon dioxide systems.
562 Therefore, hydrate preventive techniques using glycerol, diethylene glycol and triethylene glycol
563 can be replaced with amino acids as they are efficient and environmentally friendly. However,
564 amino acids are less soluble at high concentrations which might be a limiting factor to their
565 application in large concentrations. Proline is proven to have to exhibit wide solubility in water
566 for hydrate mitigation applications (Sa et al., 2016).

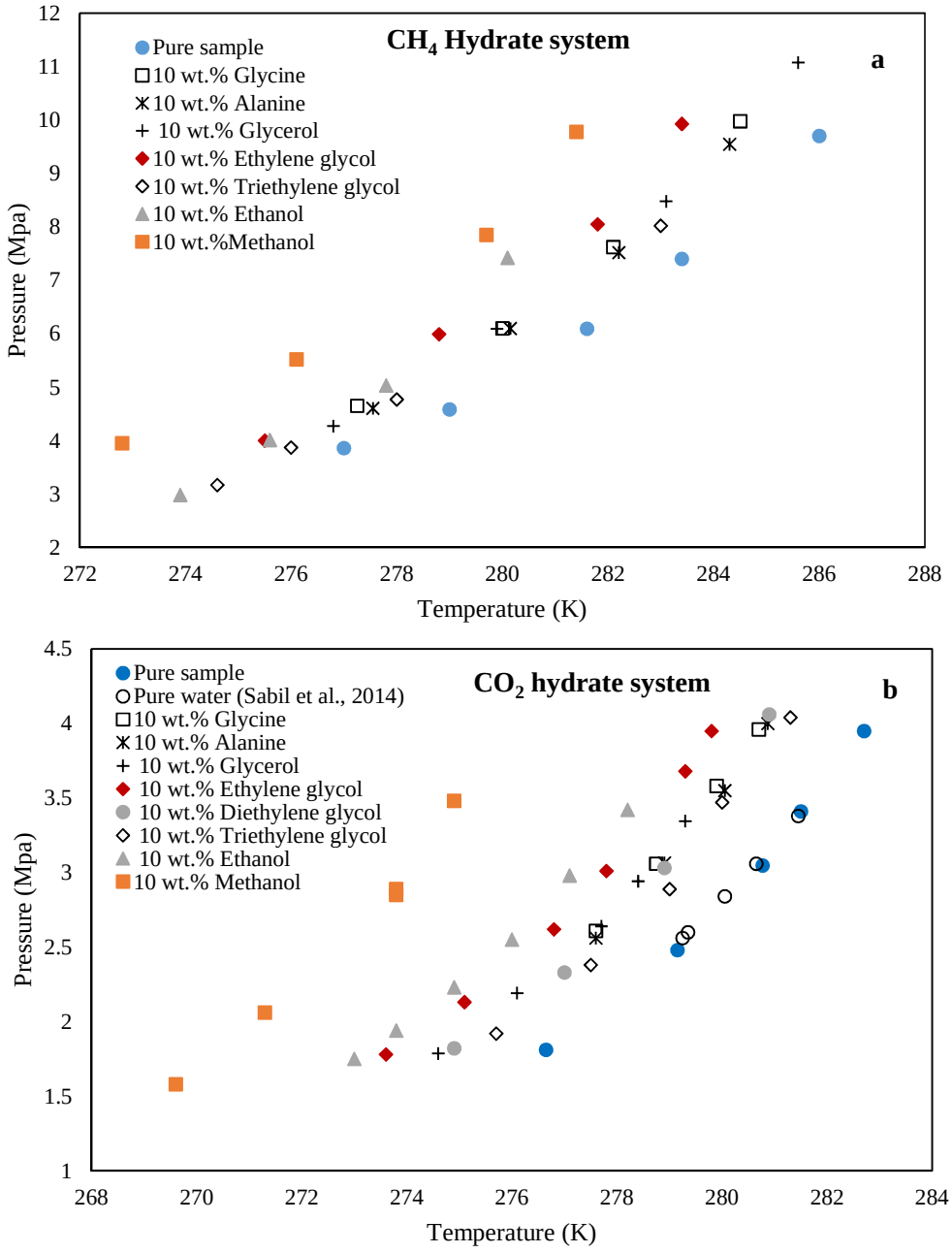

Figure 9. Comparison of the THI efficiency of amino acids and conventional additives for CH_4 and CO_2 hydrate system at 10 wt.%; the pure water data for CH_4 and CO_2 are taken from reference (Bavoh et al., 2017; Bavoh et al., 2016b; Nasir et al., 2014); (a) CH_4 hydrate system; (b) CO_2 hydrate system.

Due to different experimental and pressure conditions and equipment apparatus, the kinetic study comparison of amino acids and conventional KHIs/KHPs are compared as reported in their respective studies in literature and are tabulated in Table 4. General conventional additives are

still relatively better than amino acids as shown in Table 4. However, amino acids are still promising to explore, improve and apply in hydrate-based applications since they are environmentally friendly (Tao et al., 2006), economical (Mueller and Huebner, 2003), and demonstrate good performance potentials. In addition, amino acids can combat corrosion (Barouni et al., 2014; Hamadi et al., 2018) than the current conventional additives (Hourania and Abo-Hassan, 2016; Mustafa and Mekhamer, 2012) and are biodegradable (Fukumoto et al., 2005) and preferred to current conventional additives used in hydrate-based application. Thus, amino acids are worth studying towards commercialization.

Table 4. Comparison of the KHI/KHP efficiency of amino acids and conventional additives

Amino acid	**Remarks**	**Reference**
Commercial KPIs (SDS)		
Histidine	SDS promotes methane hydrate better than histidine at 1 wt.%.	(Bhattacharjee et al., 2016)
Leucine	leucine is not efficient as SDS in promoting methane hydrate at 0.3 wt.%.	(Veluswamy et al., 2016)
Valine	Valine is an effective methane hydrate promoter than SDS at 1 wt.%.	(Bavoh et al., 2018c)
Arginine	Arginine is a poor promoter of methane hydrate compared with SDS at 1 wt.%.	(Bavoh et al., 2018c)
Histidine	SDS is a good promoter than histidine for ethane hydrate formation. However, histidine effectively promoters methane + propane hydrate than SDS.	(Roosta et al., 2018)
Commercial KHIs (PVP/ PVCap)		
Glycine	Glycine and PVP has similar CO_2 hydrate inhibition impact efficiency.	(Sa et al., 2013)
Tyrosine	PVP is efficient than tyrosine in preventing natural gas hydrate at 1 wt.%.	(Kakati et al., 2016a)
Tyrosine	PVP is a poor inhibitor compared to tyrosine for methane + ethane hydrate at 0.02 wt.%.	(Talaghat, 2014)
Histidine	Histidine is more efficient than PVP in preventing CO_2 hydrate formation at 1.5 wt.%, but similar at 1 wt.%.	(Roosta et al., 2016)
Glycine	PVP is slight better than glycine.	(Roosta et al., 2016)
Glycine	Glycine exhibits weak hydrate formation inhibition impact compared to PVP (for pure ethane and mixed methane + propane)	(Roosta et al., 2018)
Glycine	PVCap is more efficient in prevention CH_4 hydrate formation than glycine at 1 wt.%.	(Xu et al., 2017)

4. Modeling and simulation of gas hydrate in the presence of amino acids

Presently, literatures (Bavoh et al., 2018b; Bavoh et al., 2017) have studied the thermodynamics modeling of gas hydrate inhibition in amino acids, by adopting the Dickens and Quinby-Hunt, (1997) model which is an extension of the non-electrolyte hydrate inhibitors model by Pieroen (Pieroen, 1955). The model is based on the fact that amino acids behave like salts and thus any gas hydrate model for salt model can be adopted for amino acids. Details on the model formulations and assumptions can be found in literature (Bavoh et al., 2017; Dickens and Quinby-Hunt, 1997; Pieroen, 1955). The simplified form of the model is presented in equation (1):

$$\left[\frac{1}{T_w}-\frac{1}{T_{aa}}\right]=\frac{n\Delta \mathrm{H}_{FUS(i)}}{\Delta \mathrm{H}_d}\left[\frac{1}{T_{f(i)}}-\frac{1}{T_{fa}}\right] \quad (1)$$

where $T_{f(i)}$ and T_{fa} are the freezing point temperatures of water (at 273.15 K) and water + amino acid solution, $\Delta H_{FUS(i)}$ is the heat of fusion of ice (6008 J/mol), ΔH_d is the molar enthalpy of dissociation of the gas system (which can determined experimentally or via Clausius-Clapeyron equation), n is the hydration number of the gas system (which can be determined for each gas system or taken from literature (Anderson, 2004)), R is the gas universal constant, T_w and T_{aa} are the hydrate phase boundary temperatures in pure water and water + amino acid solution, respectively. The model is able to predict hydrate phase boundary conditions for methane and carbon dioxide with AAE less than 0.2 K (Bavoh et al., 2017; Mannar et al., 2017).

However, kinetically, Naeiji et al., (2014a) and Rad et al., (2015) modeled THF and ethane hydrate formation rate adapting the thermodynamic natural path in a constant volume process. Roosta et al., (2016) recently, modeled the kinetic impact of amino acids on CO_2 hydrates using

608 a chemical affinity model. The model parameters agreed with the experimental results that the
609 rate of CO_2 hydrate formation is reduced in the presence of amino acids. In addition, molecular
610 dynamics simulation study has been reported on CH_4 hydrates by Oluwunmi et al., (2015). The
611 simulation suggests that, asparagine has the ability to inhibit hydrate formation and growth by
612 adsorbing at the water/methane interface due to its hydrophilic in nature. Furthermore,
613 Bhattacharjee et al., (2016) simulated CH_4 hydrate formation in the presence of histidine, which
614 showed good agreement with experimental results. However, the presence of histidine was found
615 to promote CH_4 hydrate formation. A recent MD simulation on the methane hydrate inhibition
616 impact of glycine, proline, serine, and alanine confirms their KHI behavior (Maddah et al.,
617 2018). The study was conducted by evaluating parameters such as the radial distribution
618 function, four-body structural order parameter, potential energy, mean square displacement,
619 density, and hydrogen bond formation. The study reported that the instability of structure I gas
620 hydrate structure responsible for methane hydrate inhibition is due to the van der Waals,
621 potential energy, and electrostatic force of interactions amongst each amino acid and water
622 molecules in the solution. The Conductor like Screening Model for Real Solvents (COSMO-RS)
623 software (Bavoh et al., 2016a; Khan et al., 2016; Klamt, 2016, 2011), an effective and fast
624 method of screening compounds/additives have been proposed as an efficient tool for screen
625 amino acids for gas hydrate studies via hydrogen bonding energies and sigma profile/potential
626 predictions (Bavoh et al., 2017, 2016b).

627 **5. Recommendations for further studies**

628 Amino acids have demonstrated strong and encouraging potentials of being efficient in various
629 gas hydrate-based technologies which may lead to commercialization. Despite weakness in
630 promoting hydrate thermodynamically, they have good hydrate thermodynamic and kinetic

inhibition potentials and very efficient in kinetically promoting hydrate formation for natural gas storage, CO_2 capture and gas separation. In addition, they are relatively less costly, biodegradable, environmentally friendly, noncorrosive, and do not produce foams, hence very promising for future industrial gas hydrate-based technology applications. However, to usefully apply amino acids, their hydrate inhibition and promotion efficient must be enhanced to meet industrial requirements. Current studied amino acids do not effectively inhibit and promote gas hydrate formation compared with the conventional additives used by the industry. Hence research towards amino acids commercialization in hydrate-based technology should focus on:

- The improvement of amino acids hydrate inhibition and promotion effect (both kinetic and thermodynamic) by conducting more laboratory investigations on new amino acids on different hydrate formers, with special attention on unnatural amino acids. Since there are huge data base of unnatural amino acids that have not been studied.
- In addition, synergic studies involving amino acids and conventional additives or other novel gas hydrate additives (such as ionic liquids etc.) may also aid boost amino acids efficient in various gas hydrate-based technologies.
- Studies and enhancement of amino acids effect of gas hydrate stability and selectivity (as amino acids inhibition of promotion effect is gas composition dependant). This will be very useful in natural gas storage and gas separation application technologies.
- More molecular level experimentations and simulations to aid understand the amino acids hydrate formation inhibition and/or promotion effect of amino acids hydropathy, acidity, polarity, and structure are highly need. These will give more understanding and insight in screening amino acids for hydrate-based technologies. Furthermore, molecular level understanding on the influence of amino acids on gas hydrate cage occupancy and

storage capacity will be needed for CO_2 capture and hydrate storage technology development.

- Regardless of the positive environmental impact of amino acids, the Cost comparison between amino acids and conventional promoters/inhibitors are need for their industrial consideration. Furthermore, considering amino acids as promoters for CO_2 capture and sequestration and gas storage and transportation pilot scale testing will be a positive step towards commercialization.
- Laboratory scale Pilot testing of amino acids will be a step towards commercialization. Specifically, in flow assurance, flow loop testing of amino acids in brine water in natural gas system at low and high amino acids concentrations is highly recommended for industrial applications. In addition, some hydrate inhibitors are not compatible with other industrial additives (e.g. corrosion inhibitors) (Kamal et al., 2016; Kelland, 2006; Kelland et al., 2000). Their application affects the performance of such additives, thus performing compatibility test of amino acids and other industrial additives coupled with economic analysis is important in paving way for the successful application of amino acids in gas hydrate-based application.

6. Conclusion

The influence of amino acids on gas hydrate formation have been reviewed based on available data in open literature. Based on the review, it is concluded that: most amino acids promote hydrate formation kinetics, while few (glycine and alanine) inhibit gas hydrate thermodynamically as well as kinetically, thus, they act as dual functional inhibitors, similarly to ILs. Amino acids are generally THIs with no thermodynamic promotion reported. Amino acids

promotion/inhibition effect greatly depends on their respective side chain properties (hydropathy, side chain alkyl, length polarity, functional group, etc.), solubility, concentration, studied concentration units, interaction between the guest molecule, and hydrogen bond and electrostatic force of attraction with water molecules. However, amino acids hydropathy is less understood, resulting in difficulty in correlating available hydropathy scales with gas hydrate inhibition impact. Amino acids are generally gas hydrate kinetic promoters, but some amino acids slightly inhibit gas hydrate kinetically by perturbing the local water structure and lattice distortion and expansion by incorporation into hydrate lattice crystals. In addition, the effect of amino acids on hydrate structures characterization is needed for modelling (thermodynamic and kinetic modelling) purposes. Finally, more MD simulation is needed to understand gas hydrate inhibition mechanism in amino acids. Amino acids are potential additive for future hydrate-based applications especially in CO_2 capture and storage and natural gas storage.

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List of Tables

Table 1. List of various studied amino acids + studied gas systems, concentrations used and physicochemical properties.

No	Amino Acid	Gas	Side chain Polarity	Side chain	Hydropathy index[d]	Test type	Conc.[a,b,c]	Remarks	Ref.
1	Glycine	CO_2	Nonpolar	-H	-0.4	THI	0.1[a] – 3.0[a]	Shows good thermodynamic hydrate inhibition impact.	(Sa et al., 2011)
2	L-Alanine	CO_2	Nonpolar	$-CH_3$	1.8	THI	0.1[a] – 2.2[a]	Thermodynamically inhibit CO_2 hydrates	
3	L-Valine	CO_2	Nonpolar	$-CH(CH_3)_2$	4.2	THI	0.1[a] – 0.5[a]	Shows thermodynamic CO_2 hydrate inhibition	
4	Glycine	CO_2	Nonpolar	-H	- 0.4	KHI	0.01[a] – 1.0[a]	Shows effective KHI impact by increasing the subcooling temperature and can eliminate the memory effect.	(Sa et al., 2013)
5	L-Alanine	CO_2	Nonpolar	$-CH_3$	1.8	KHI	0.1[a]	Demonstrates kinetic hydrate inhibition impact but less efficient than glycine.	
6	L-Valine	CO_2	Nonpolar	$-CH(CH_3)_2$	4.2	KHI	0.1[a]	Shows very less significant hydrate inhibition impact. Longer chins which are more hydrophobic do not inhibit hydrate. This is contrary to the understanding that hydrophobic compounds turns to be good KHIs (especially in ionic liquids (Tariq et al., 2014))	
7	Leucine	CO_2	nonpolar	$-CH_2CH(CH_3)$	3.8	KHI	0.1[a]	Shows very less significant hydrate inhibition impact.	
8	Isoleucine	CO_2	nonpolar	$-CH(CH_3)C_2H_5$	4.5	KHI	0.1[a]	Shows very less significant hydrate inhibition impact.	
9	Glycine	CO_2	nonpolar	-H	-0.4	Crystal structure	0.1[a] – 0.5[a]	Amino acids inclusion expands the hydrate crystal lattice, causing hydrate inhibition effect. At 2.2 mol% glycine's lattice expansion ability saturation is reached.	(Sa et al., 2014)
10	L-Alanine	CO_2	nonpolar	$-CH_3$	1.8	Crystal structure	0.1[a] – 0.5[a]	A structure I hydrate was formed with hydrate inhibition crystallization phenomenon. The lattice expansion magnitude was saturated at 0.5 mol%	
11	L-Valine	CO_2	nonpolar	$-CH(CH_3)_2$	4.2	Crystal structure	0.1[a] – 0.5[a]	All amino acids have a distinct crystal structure. However, the inhibition strength of amino acids depends on whether they act individually or agglomerate during hydrate crystallization.	
12	L-Alanine	CO_2	nonpolar	$-CH_3$	1.8	KHI + spectroscopy	0.01[a] – 0.1[a]	Delays hydrate nucleation and growth rate via disruption of the water structure in hydrate formation.	(Sa et al., 2015)

13	Aspartic acid	CO_2	acidic polar	$-CH_2COOH$	− 3.5	KHI + spectroscopy	0.01[a]	Delays hydrate nucleation and growth rate better than alanine but similar to asparagine via disruption of the water structure in hydrate formation.	
14	Asparagine	CO_2	polar	$-CH_2CONH_2$	− 3.5	KHI + spectroscopy	0.01[a]	Delays hydrate nucleation and growth rate via disruption of the water structure in hydrate formation.	
15	Phenylalanine	CO_2	nonpolar	$-CH_2C_6H_5$	2.8	KHI + spectroscopy	0.1[a]	Relatively shows no effect on the nucleation kinetics of hydrate formation, especially in memory water, due to its water structure hydrogen bonding strengthening ability. However, delays growth process but less than alanine.	
16	Histidine	CO_2	basic polar	$-CH_2C_3H_3N_2$	− 3.2	KHI + spectroscopy	0.1[a]	Efficient in hydrate inhibition than alanine but less than aspartic acid and asparagine via disruption of the water structure in hydrate formation.	
17	Glycine	C_2H_6	nonpolar	-H	- 0.4	KHI	0.05[b] – 3[b]	Shows strong KHI strength due to its lower hydrophobicity	(Rad et al., 2015)
18	Leucine	C_2H_6	nonpolar	$-CH_2CH(CH_3)$	3.8	KHI	0.05[b] – 3[b]	Inhibits hydrate formation kinetics but less than glycine.	
19	Asparagine	CH_4	polar	$-CH_2CONH_2$	− 3.5	KHI + MD simulation		Efficiently suppress hydrate formation kinetics. Asparagine do not adsorb on the gas/water interface during hydrate inhibition.	(Oluwunmi et al., 2015)
20	Glycine	THF	nonpolar	-H	- 0.4	KHI	0.05[b] - 1.5[b]	Shows strong KHI strength due to its lower hydrophobicity	(Naeiji et al., 2014a)
21	Leucine	THF	nonpolar	$-CH_2CH(CH_3)$	3.8	KHI	0.05[b] - 1.5[b]	Inhibits hydrate formation kinetics but less than glycine.	
22	L-threonine	CH_4	polar	$-CH(OH)CH_3$	− 0 .7	KHI	2770[c] - 1385[c]	Shows no significant KHI effect in delaying hydrate nucleation in both fresh and memory system.	(Perfeldt et al., 2014)
23	L-valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	KHI	2770[c] - 1385[c]	Shows no significant KHI effect in delaying hydrate nucleation in both fresh and memory system.	
24	L-histidine	CH_4	Basic polar	-NH-CH=N-CH=C-CH2	-3.2	KHI	0.1[b] – 1[b]	Significantly promotes hydrate formation than SDS.	(Bhattacharjee et al., 2016)
25	PVP and L-Tyrosine	NG	Polar	$-HO-Ph-CH_2$	-1.3	KHI	1[b]	The presence of tyrosine improves the hydrate inhibition impact of NaCl + PVP system.	(Kakati et al., 2016a)
26	PVP and L-Tyrosine	NG	Polar	$-HO-Ph-CH_2$	-1.3	KHI	100[c] – 275[c]	Tyrosine is a strong inhibitor than PVP and its addition into PVP enhances hydrate nucleation time in several folds.	(Talaghat, 2014)
27	Glycine	CH_4	nonpolar	-H	-0.4	THI	0.5[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	(Sa et al., 2016)
28	Alanine	CH_4	nonpolar	$-CH_3$	1.8	THI	0.5[a] – 2.2[a]	Inhibits hydrate phase boundary curve with concentration.	

29	Serine	CH_4	polar	-HO-CH_2	-0.8	THI	1.3[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	
30	Proline	CH_4	nonpolar	-NH-$(CH_2)_3$	-1.6	THI	1.3[a] – 9[a]	Inhibits hydrate phase boundary curve with concentration.	
31	Glycine	CH_4	nonpolar	-H	-0.4	KHI	0.1[a]	Exhibits hydrate nucleation time and growth rate delay in both fresh and memory water	
32	Alanine	CH_4	nonpolar	-CH_3	1.8	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
33	Serine	CH_4	polar	-HO-CH_2	-0.8	KHI	0.1[a]	Exhibits hydrate nucleation time and growth rate delay in both fresh and memory water	
34	Proline	CH_4	nonpolar	-NH-$(CH_2)_3$	-1.6	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
35	Glycine	NG	nonpolar	-H	-0.4	THI	0.5[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	
36	Alanine	NG	nonpolar	-CH_3	1.8	THI	0.5[a] – 2.2[a]	Inhibits hydrate phase boundary curve with concentration.	
37	Serine	NG	polar	-HO-CH_2	-0.8	THI	1.3[a] – 3[a]	Inhibits hydrate phase boundary curve with concentration.	
38	Proline	NG	nonpolar	-NH-$(CH_2)_3$	-1.6	THI	1.3[a] – 9[a]	Inhibits hydrate phase boundary curve with concentration.	
39	Glycine	NG	nonpolar	-H	-0.4	KHI	0.1[a]	Exhibits hydrate nucleation time and growth rate inhibition effect.	
40	Alanine	NG	nonpolar	-CH_3	1.8	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
41	Serine	NG	polar	-HO-CH_2	-0.8	KHI	0.1[a]	Could inhibit hydrate formation kinetics better than glycine	
42	Proline	NG	nonpolar	-NH-$(CH_2)_3$	-1.6	KHI	0.1[a]	Do not inhibit hydrate formation nucleation and growth rate	
43	Glycine	CO_2	nonpolar	-H	-0.4	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate with increasing concentration	(Roosta et al., 2016)
44	Proline	CO_2	nonpolar	-NH-$(CH_2)_3$	-1.6	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate with inhibition strength less than glycine but similar with serine and threonine.	
45	Serine	CO_2	polar	-HO-CH_2	-0.8	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate	
46	Threonine	CO_2	polar	CH_3-CH(OH)	-0.7	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate	
47	Glutamine	CO_2	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI	0.5[b] – 2[b]	Inhibits hydrate formation rate with the least inhibition strength compared with other studied amino acids.	
48	Histidine	CO_2	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI	0.5[b] – 2[b]	Shows the highest hydrate formation inhibition impact compared with other studies amino acids.	
49	Glycine	CH_4	nonpolar	-H	-0.4	THI	5[b] – 20[b]	Shows the highest hydrate phase behavior conditions inhibition compared with other studied amino acids.	(Bavoh et al., 2016b)

50	Alanine	CH_4	nonpolar	$-CH_3$	1.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
51	Serine	CH_4	polar	$-HO-CH_2$	-0.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
52	Proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	THI	10^b	Inhibits gas hydrate thermodynamically.	
53	Arginine	CH_4	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	THI	10^b	Inhibits gas hydrate thermodynamically.	
54	Glycine	CO_2	nonpolar	-H	-0.4	THI	$5^b – 20^b$	Shows the highest hydrate phase behavior conditions inhibition compared with other studied amino acids.	(Bavoh et al., 2017)
55	Alanine	CO_2	nonpolar	$-CH_3$	1.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
56	Serine	CO_2	polar	$-HO-CH_2$	-0.8	THI	10^b	Inhibits gas hydrate thermodynamically.	
57	Proline	CO_2	nonpolar	$-NH-(CH_2)_3$	-1.6	THI	10^b	Inhibits gas hydrate thermodynamically.	
58	Arginine	CO_2	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	THI	10^b	Inhibits gas hydrate thermodynamically.	
59	L-Leucine	CH_4	nonpolar	$-CH_2CH(CH_3)$	3.8	KHP/morphology	$0.1^b – 0.5^b$	Shows kinetic promotion with no promotion effect observed below 0.3 wt%.	(Veluswamy et al., 2016)
60	L- Methionine	CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP	$0.02^b – 1^b$	Significantly promotes hydrate formation uptake without the use of energy-intensive mixing.	(Cai et al., 2017)
61	L-norvaline	CO_2	nonpolar	C10H19NO4	-	KHP	$0.02^b – 1^b$	Promotes hydrate formation with similar promotion impact as L-norleucine	
62	L-norleucine	CO_2	nonpolar	C6H13NO2	-	KHP	$0.02^b – 1^b$	Promotes hydrate formation	
63	2-aminoheptanoic acid	CO_2	acid	C7H15NO2	-	KHP	$0.02^b – 1^b$	Promotes hydrate formation but with less promotion impact compared with L-norleucine	
64	n-hexanoic acid	CO_2	acid	CH 3 4COOH	-	KHP	$0.02^b – 1^b$	Promotes hydrate formation with similar promotion impact as 2-aminoheptanoic acid	
65	n-hexylamine	CO_2	nonpolar	CH3CH2CH2CH2CH2CH2NH2	-	KHP	$0.02^b – 1^b$	Promotes hydrate formation	
66	L-tryptophan	CH_4	nonpolar	Ph-NH-CH=C-CH2-	-0.9	KHP	$0.01^b – 0.3^b$	Shows good kinetic hydrate formation enhancement effect in both stirred and unstirred systems.	(Veluswamy et al., 2017)
67	L-histidine	CH_4	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHP	$0.03^b – 1^b$	Shows hydrate formation promotion effect similar to arginine but less than tryptophan. Higher hydrophobic amino acids show less hydrate promotion effect.	

68	L-arginine	CH_4	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	KHP	0.03^b – 1^b	Shows hydrate formation promotion effect	
69	Lysine	CH_4	basic polar	H2N-(CH2)4-	-3.9	THI	5^b -10^b	Shows THI effect with increasing concentration.	(Mannar et al., 2017)
70	Lysine	CO_2	basic polar	H2N-(CH2)4-	-3.9	THI	5^b -10^b	Shows THI effect with increasing concentration.	
71	Arginine	CH_4	basic polar	HN=C(NH2)-NH-(CH2)3	-4.5	THI/KHP	1^b – 5^b	Slightly inhibits methane hydrate phase boundary as well as promoting hydrate formation uptake	(Bavoh et al., 2018c)
72	Valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	THI/KHP	1^b – 5^b	Slightly inhibits methane hydrate phase boundary as well as promoting hydrate formation uptake. Shows high uptake than arginine.	
73	Valine,	CO_2	nonpolar	$-CH(CH_3)_2$	4.2	KHP	0.5^b	Promotes hydrate formation uptake about 1.2 times.	(Prasad and Kiran, 2018a)
74	Phenylalanine	CO_2	nonpolar	Ph-CH2-	2.8	KHP	0.5^b	Shows no significant hydrate promotion effect	
75	Cysteine	CO_2	nonpolar	HS-CH2-	2.5	KHP	0.5^b	Promotes hydrate formation uptake about 1.2 times.	
76	Methionine	CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP	0.5^b	Promotes hydrate formation uptake about 1.2 times.	
77	Threonine	CO_2	polar	CH_3-CH(OH)	-0.7	KHP	0.5^b	Shows no significant hydrate promotion effect	
78	Methionine	CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP/XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	(Prasad and Kiran, 2018)
79	Phenylalanine	CO_2	nonpolar	Ph-CH2-	2.8	KHP/ XRD	0.5^b	Shows less hydrate kinetics conversion rate, thus gives less hydrate formation uptake.	
80	Methionine	CH_4	nonpolar	CH3-S-(CH2)2-	1.9	KHP/XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
81	Phenylalanine	CH_4	nonpolar	Ph-CH2-	2.8	KHP/ XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
82	Methionine	CH_4 + CO_2	nonpolar	CH3-S-(CH2)2-	1.9	KHP/XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
83	Phenylalanine	CH_4 + CO_2	nonpolar	Ph-CH2-	2.8	KHP/ XRD	0.5^b	Shows efficient hydrate kinetics conversion rate, thus improving the hydrate formation uptake.	
84	Glycine + ethylene glycol	CH_4	nonpolar	-H	-0.4	THI	1^b – 30^b 1:1 mixtures	Glycine can enhance the thermodynamic inhibition strength of ethylene glycol, shows strong synergic inhibition effect.	(Long et al., 2018)
85	Glycine	CH_4	nonpolar	-H	-0.4	MD simulation	0.45^b - 1.5^b	Shows hydrate kinetics inhibition effect but less than serine.	(Maddah et

86	Alanine	CH_4	nonpolar	$-CH_3$	1.8	MD simulation	0.45^b - 1.5^b	Shows hydrate kinetics inhibition	al., 2018)
87	Serine	CH_4	polar	$-HO-CH_2$	-0.8	MD simulation	0.45^b - 1.5^b	Shows efficient hydrate kinetics inhibition via interruption of the hydrogen bond network of water.	
88	Proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	MD simulation	0.45^b - 1.5^b	Shows hydrate kinetics inhibition effect as alanine	
89	L-leucine	CH_4 and NG	nonpolar	$-CH_2CH(CH_3)$	3.8	KHP	0.1^b – 1^b	Very efficient in promoting hydrate formation kinetics than all studied amino acids at low concentrations for both structure I and structure II natural gas hydrates systems.	(Liu et al., 2015)
90	L-isoleucine	CH_4	nonpolar	$-CH(CH_3)C_2H_5$	4.5	KHP	0.5^b	Exhibits good hydrate promotion ability similar to phenylalanine.	
91	L-valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	KHP	0.5^b	Enhances hydrate formation kinetics.	
92	L-threonine	CH_4	polar	$CH_3-CH(OH)$	-0.7	KHP	0.5^b -10^b	Enhances hydrate formation with decreasing concentration.	
93	L-alanine	CH_4	nonpolar	$-CH_3$	1.8	KHP	0.5^b -2^b	Exhibits negligible hydrate promotion effect with increasing concentration.	
94	L-proline	CH_4	nonpolar	$-NH-(CH_2)_3$	-1.6	KHP	0.5^b	Exhibits less hydrate promotion effect.	
95	L-methionine	CH_4	nonpolar	$CH3-S-(CH2)_2-$	1.9	KHP	0.5^b	Shows good hydrate promoters strength.	
96	L-tryptophan	CH_4	nonpolar	Ph-NH-CH=C-CH_2-	-0.9	KHP	0.5^b	Shows good hydrate promoters strength.	
97	L-phenylalanine	CH_4	nonpolar	Ph-CH_2-	2.8	KHP	0.5^b	Shows good hydrate promoters strength.	
98	L-arginine	CH_4	basic polar	$HN=C(NH_2)-NH-(CH2)_3$	-4.5	KHP	0.5^b	Able to promote hydrate formation kinetics with decreasing stability.	
99	L-glutamic acid	CH_4	acidic polar	$HOOC-(CH_2)_2-$	−3.5	KHP	0.5^b	Able to promote hydrate formation kinetics with decreasing stability.	
100	L-histidine	CH_4	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHP	0.5^b	Able to promote hydrate formation kinetics with decreasing stability.	
101	L-serine	CH_4	polar	$-HO-CH_2$	-0.8	KHP	0.5^b	Exhibits less hydrate promotion effect	
102	L-aspartic acid	CH_4	acidic polar	$-CH_2COOH$	− 3.5	KHP	0.5^b	Exhibits less hydrate promotion effect	
103	L-valine	CH_4	nonpolar	$-CH(CH_3)_2$	4.2	THI	1^b – 5^b	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	(Bavoh et al., 2018a)
104	L-threonine	CH_4	polar	$CH_3-CH(OH)$	-0.7	THI	1^b – 5^b	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	

105	Asparagine	CH_4	polar	$-CH_2CONH_2$	− 3.5	THI	$1^b – 5^b$	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	
106	L-phenylalanine	CH_4	nonpolar	Ph-CH_2-	2.8	THI	$1^b – 5^b$	Shows less thermodynamic hydrate inhibition, however may increase with concentration depending on its solubility.	
107	Glycine	C_2H_6	nonpolar	-H	-0.4	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
108	L-serine	C_2H_6	polar	-HO-CH_2	-0.8	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
109	L-histidine	C_2H_6	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
110	Glutamine	C_2H_6	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI/KPI	$0.5^b – 1.5^b$	Exhibit promotion effect	
111	Glycine	CH_4 + C_3H_8	nonpolar	-H	-0.4	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect and enhances the inhibition effect of PVP more than serine	
112	L-serine	CH_4 + C_3H_8	polar	-HO-CH_2	-0.8	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect but slightly enhances PVP hydrate inhibition impact.	
113	L-histidine	CH_4 + C_3H_8	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	(Roosta et al., 2018)
114	Glutamine	CH_4 + C_3H_8	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI/KPI	$0.5^b – 1.5^b$	Exhibit promotion effect	
115	Glycine	CH_4 + THF	nonpolar	-H	-0.4	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
116	L-serine	CH_4 + THF	polar	-HO-CH_2	-0.8	KHI/KPI	$0.5^b – 1.5^b$	Exhibit hydrate inhibition effect	
117	L-histidine	CH_4 + THF	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHI/KPI	$0.5^b – 1.5^b$	Exhibit weak hydrate inhibition effect	
118	Glutamine	CH_4 + THF	polar	H_2N-CO-$(CH_2)_2$	-3.5	KHI/KPI	$0.5^b – 1.5^b$	No significant effect	
119	Glycine	CH_4	nonpolar	-H	-0.4	KHI	$1^b – 7^b$	Poor kinetic hydrate inhibitor on the bases of induction time and hydrate formation onset temperature even at high concentrations.	(Xu et al., 2017)
120	PVCap + Glycine	CH_4 + THF	nonpolar	-H	-0.4	KHI	$1^b : 1^b – 5^b$	Efficiently improves PVCap hydrate inhibition strength to about 16 time.	
121	Glycine	CH_4	nonpolar	-H	-0.4	KHDP	$0.01^b – 5^b$	Efficiently enhances methane hydrate dissociation kinetics.	(Kumar et

122	L-serine	CH_4	polar	-HO-CH_2	-0.8	KHDP	0.01[b] – 5[b]	Enhances methane hydrate dissociation kinetics.	al., 2017)
123	L-histidine	CH_4	basic polar	NH-CH=N-CH=C-CH_2	-3.2	KHDP	0.01[b] – 5[b]	Efficiently enhances methane hydrate dissociation kinetics, with high methane recovery potential.	
124	L-threonine	CH_4	polar	CH_3-CH(OH)	-0.7	KHDP	0.01[b] – 5[b]	Enhances methane hydrate dissociation kinetics.	
125	L-tryptophan	CH_4	nonpolar	Ph-NH-CH=C-CH_2-	-0.9	KHDP	0.01[b] – 5[b]	Enhances methane hydrate dissociation kinetics.	
126	L-threonine	CH_4	polar	CH_3-CH(OH)	-0.7	KHDP	0.01[b] – 5[b]	Enhances methane hydrate dissociation kinetics.	
127	Proline	CH_4	nonpolar	-NH-$(CH_2)_3$	-1.6	KHDP	0.01[b] – 5[b]	Poorly enhances methane hydrate dissociation kinetics.	
128	Glycine + 1-Ethyl-3-methy-limidazolium chloride	CH_4	nonpolar	-H	-0.4	THI	5[b] + 5[b]	Glycine + 1-Ethyl-3-methy-limidazolium chloride has negligible effect on their pure system phase boundary. However, they inhibit methane hydrate formation.	(Bavoh et al., 2018c)

[a] mol%; [b] wt.%; [c] ppm; [d]extracted from reference (Kyte and Doolittle, 1982);
THI refers to Thermodynamic hydrate inhibitor; THP refers to Thermodynamic hydrate promoter; KHI refers to Kinetic hydrate inhibitor; KHP refers to Kinetic hydrate promoter; KHDP refers to Kinetic hydrate dissociation promoter.

Table 2. Amino acids HL_wVE data

Author	**Amino acid**	**Gas**	**Conc./ mol%**	**T/K**	**P/MPa**	**Data points**
Sa *et al*., 2011 (Sa et al., 2011)	Glycine	CO_2	0.1	274.55 -281.35	1.49-3.51	5
		CO_2	0.5	274.35-281.05	1.49-3.50	5
		CO_2	1.3	273.85-280.65	1.49-3.51	5
		CO_2	2.2	273.35-280.15	1.44-3.48	5
		CO_2	3	273.05-279.45	1.47-3.47	5
	Alanine	CO_2	0.1	274.55-281.45	1.49-3.52	5
		CO_2	0.5	274.25-280.95	1.48-3.49	5
		CO_2	1.3	273.75-280.35	1.47-3.49	5
		CO_2	2.2	273.25-279.95	1.46-3.48	5
	Valine	CO_2	0.1	274.45-281.35	1.48-3.51	5
		CO_2	0.5	274.15-280.85	1.48-3.50	5
Sa *et al*., 2016 (Sa et al., 2016)	Glycine	CH_4	0.5	274.45-284.85	2.940-8.965	5
		CH_4	1.3	273.95-284.30	2.953-8.93	5
		CH_4	2.2	273.35-283.75	2.942-8.923	5

		CH_4	3	272.85-283.05	2.916-8.871	5
		NG	0.5	276.25-286.75	1.248-4.086	5
		NG	1.3	275.85-286.45	1.243-4.103	5
		NG	2.2	275.45-285.95	1.247-4.088	5
		NG	3	274.85-285.35	1.245-4.07	5
	Alanine	CH_4	0.5	274.25-284.85	2.947-8.952	5
		CH_4	1.3	273.95-284.15	2.953-8.928	5
		CH_4	2.2	273.05-283.58	2.932-8.914	5
		NG	0.5	276.15-286.65	1.251-4.102	5
		NG	1.3	275.75-286.35	1.245-4.106	5
		NG	2.2	285.75-275.15	1.237-4.086	5
	Serine	CH_4	1.3	273.75-284.05	2.938-8.94	5
		CH_4	3	272.65-282.85	2.937-8.889	5
		NG	1.3	274.85-285.45	1.241-4.066	5
		NG	3	273.65-283.75	1.234-4.055	5
	Proline	CH_4	1.3	283.85-273.65	8.934-2.941	5
		CH_4	3	272.3-282.50	2.929-8.868	5
		CH_4	6	268.40-278.65	28.87-8.698	5
		CH_4	9	264.90-274.00	2.839-8.473	5
		NG	1.3	274.85-285.45	1.241-4.066	5
		NG	3	273.65-283.75	1.234-4.055	5
		NG	6	270.75-280.65	1.235-3.995	5
		NG	9	267.65-276.75	1.206-3.932	5
Bavoh et al., (2016b)	Glycine	CH_4	5 wt%	277.90-285.20	4.550-9.840	4
		CH_4	10 wt%	277.25-284.50	4.650-9.980	4
		CH_4	15 wt%	276.80-283.73	4.600-9.650	4
		CH_4	20 wt%	276.50-283.10	4.800-9.770	4
	Alanine	CH_4	10 wt%	277.55-284.30	4.605-9.550	4
	Serine	CH_4	10 wt%	277.70-285.00	4.595-9.800	4
	Proline	CH_4	10 wt%	277.60-284.85	4.550-9.820	4
	Arginine	CH_4	10 wt%	278.55-285.40	4.700-9.650	4
Bavoh et al., (2017)	Glycine	CO_2	5 wt%	278.30-281.45	2.600-3.980	4
		CO_2	10 wt%	277.60-280.70	2.610-3.960	4
		CO_2	15 wt%	276.60-279.80	2.550-3.960	4
		CO_2	20 wt%	275.60-279.20	2.520-3.960	4
	Alanine	CO_2	10 wt%	277.60-280.87	2.560-4.000	4
	Serine	CO_2	10 wt%	278.20-281.30	2.600-4.000	4
	Proline	CO_2	10 wt%	277.70-281.10	2.530-4.020	4

	Arginine	CO_2	10 wt%	278.30-281.50	2.560-3.970	4
Mannar et al., (2017)	Lysine	CO_2	5 wt%	276.20-281.80	2.200- 4.010	4
		CO_2	10 wt%	276.45-281.03	2.000- 4.010	4
		CH_4	5 wt%	278.15-285.62	4.600-10.01	4
		CH_4	10 wt%	278.05-285.20	4.900-10.40	4
Bavoh et al., (2018b)	Arginine	CH_4	5 wt%	278.80-285.90	4.550-9.840	4
	Valine	CH_4	5 wt%	278.60-285.80	4.600-9.650	4
Long et al., (2018)	Glycine + ethylene glycol	CH_4	0.5 wt% + 0.5 wt%	279.70-287.80	5.050-12.20	5
	Glycine + ethylene glycol	CH_4	2.5 wt% + 2.5 wt%	279.10-286.70	5.110-11.98	5
	Glycine + ethylene glycol	CH_4	5 wt% + 5 wt%	277.10-285.40	4.780-11.47	5
	Glycine + ethylene glycol	CH_4	10 wt% + 10 wt%	274.70-282.20	4.880-11.47	5
	Glycine + ethylene glycol	CH_4	15 wt% + 15 wt%	273.30-279.90	4.810-11.15	5
Bavoh et al., (2018a)	Valine	CH_4	1 wt.%	276.20-284.10	3.600-8.10	4
			5 wt.%	275.70-283.50	3.500-8.00	4
	threonine	CH_4	1 wt.%	278.60-286.00	4.600-10.10	4
			5 wt.%	277.00-285.70	4.000-10.20	4
	Asparagine	CH_4	1 wt.%	277.90-286.10	4.300-10.30	4
			5 wt.%	275.80-283.70	3.500-8.10	4
	Phenylalanine	CH_4	1 wt.%	276.20-284.00	3.600-8.20	4
			5 wt.%	275.90-283.90	3.600-8.00	4
(Bavoh et al., 2018c)	Glycine + 1-Ethyl-3-methy-limidazolium chloride	CH_4	5 wt% + 5 wt%	277.80-284.90	4.700-9.99	4

Table 3. Variations in some studied amino acids concentration units

Wt.%	Mol %				
	Glycine	Alanine	Proline	Serine	Valine
5	1.25	1.05	0.82	0.89	0.80
10	2.60	2.20	1.71	1.87	1.68
15	4.06	3.45	2.69	2.94	2.64
20	5.66	4.81	3.76	4.11	3.70

Table 4. Comparison of the KHI/KHP efficiency of amino acids and conventional additives

Amino acid	Remarks	Reference
Commercial KPIs (SDS)		
Histidine	SDS promotes methane hydrate better than histidine at 1 wt.%.	(Bhattacharjee et al., 2016)
Leucine	leucine is not efficient as SDS in promoting methane hydrate at 0.3 wt.%.	(Veluswamy et al., 2016)
Valine	Valine is an effective methane hydrate promoter than SDS at 1 wt.%.	(Bavoh et al., 2018c)
Arginine	Arginine is a poor promoter of methane hydrate compared with SDS at 1 wt.%.	(Bavoh et al., 2018c)
Histidine	SDS is a good promoter than histidine for ethane hydrate formation. However, histidine effectively promoters methane + propane hydrate than SDS.	(Roosta et al., 2018)
Commercial KHIs (PVP/ PVCap)		
Glycine	Glycine and PVP has similar CO_2 hydrate inhibition impact efficiency.	(Sa et al., 2013)
Tyrosine	PVP is efficient than tyrosine in preventing natural gas hydrate at 1 wt.%.	(Kakati et al., 2016a)
Tyrosine	PVP is a poor inhibitor compared to tyrosine for methane + ethane hydrate at 0.02 wt.%.	(Talaghat, 2014)
Histidine	Histidine is more efficient than PVP in preventing CO_2 hydrate formation at 1.5 wt.%, but similar at 1 wt.%.	(Roosta et al., 2016)

Glycine	PVP is slight better than glycine.	(Roosta et al., 2016)
Glycine	Glycine exhibits weak hydrate formation inhibition impact compared to PVP (for pure ethane and mixed methane + propane)	(Roosta et al., 2018)
Glycine	PVCap is more efficient in prevention CH_4 hydrate formation than glycine at 1 wt.%.	(Xu et al., 2017)

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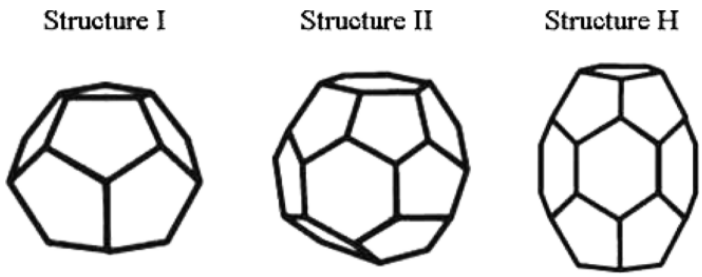


Figure 1. Common gas hydrate crystal structures (Tariq et al., 2014).

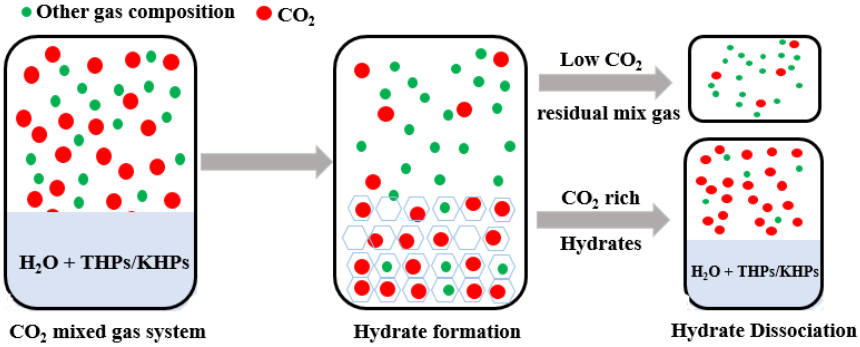
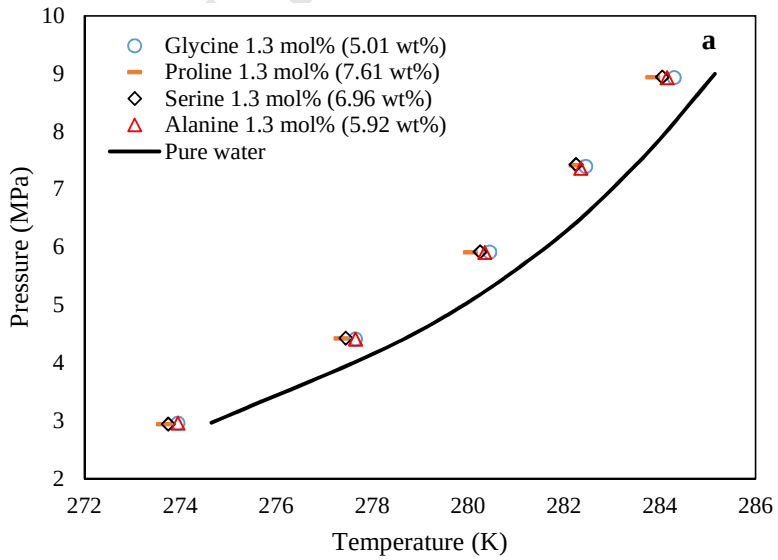
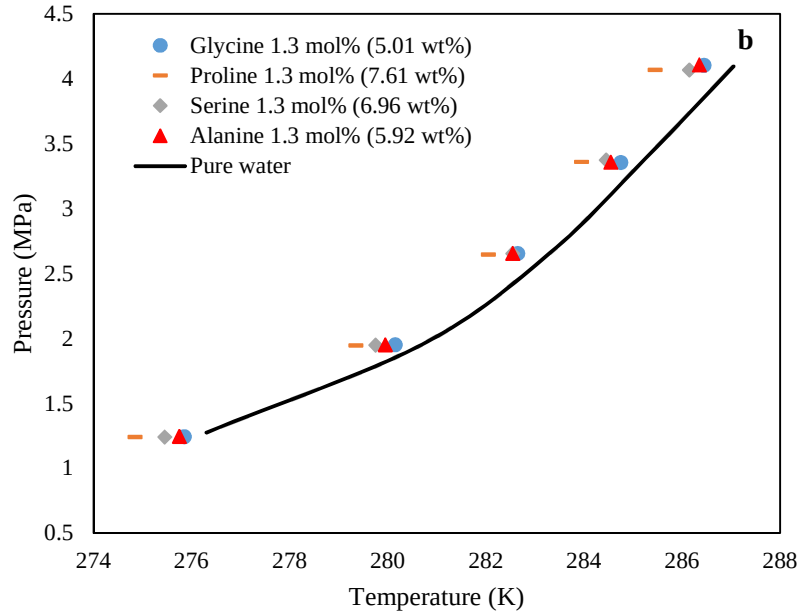


Figure 2. Hydrate-based gas separation process (CO_2 capture process) (Zheng et al., 2017)





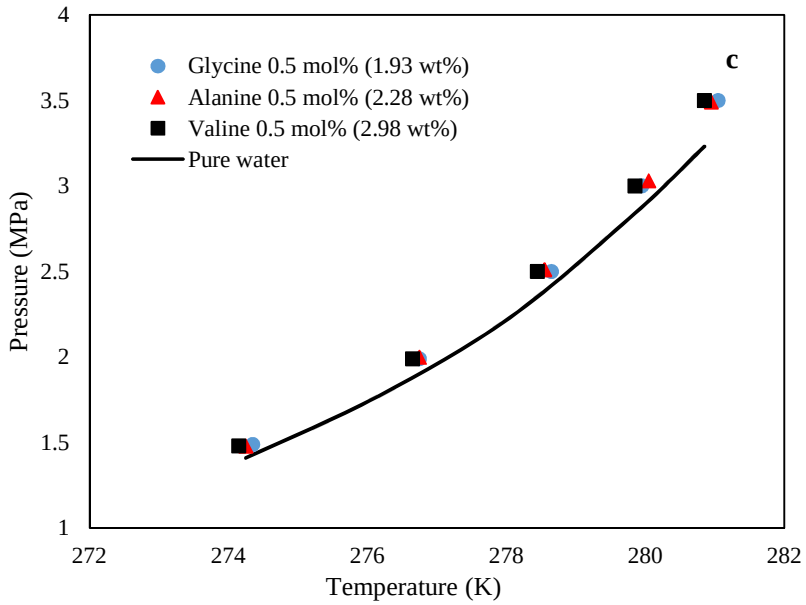


Figure 3. The inhibition strength of amino acids on the HL_wVE curve in various gas systems showing the effect of studied concentration units on inhibition impact. (a) CH_4 (Sa et al., 2016); (b) NG (Sa et al., 2016); and (c) CO_2 (Sa et al., 2011).

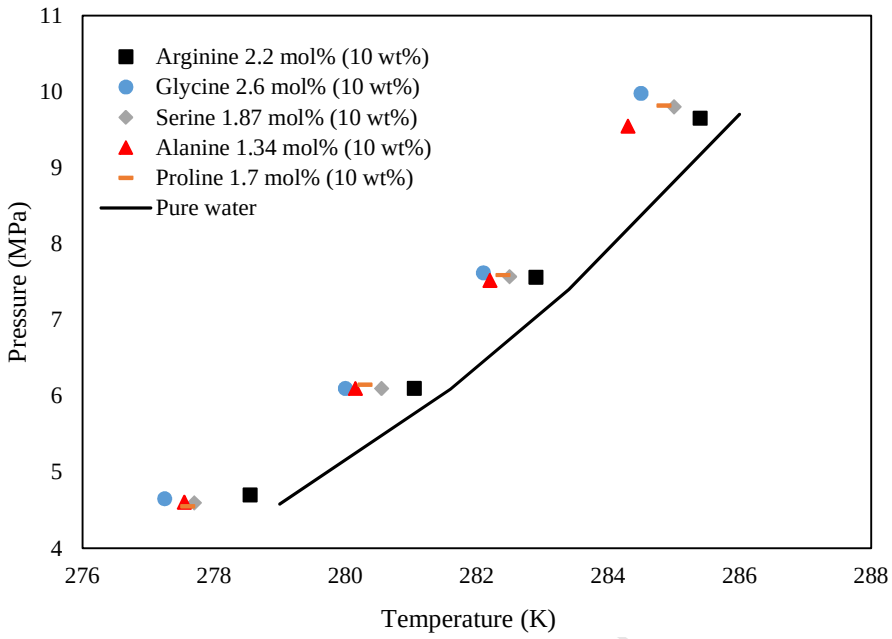


Figure 4. The inhibition impact of amino acids on the HL_wVE curve of CH_4 hydrate systems showing the effect of studied concentration units on inhibition impact (Bavoh et al., 2016b).

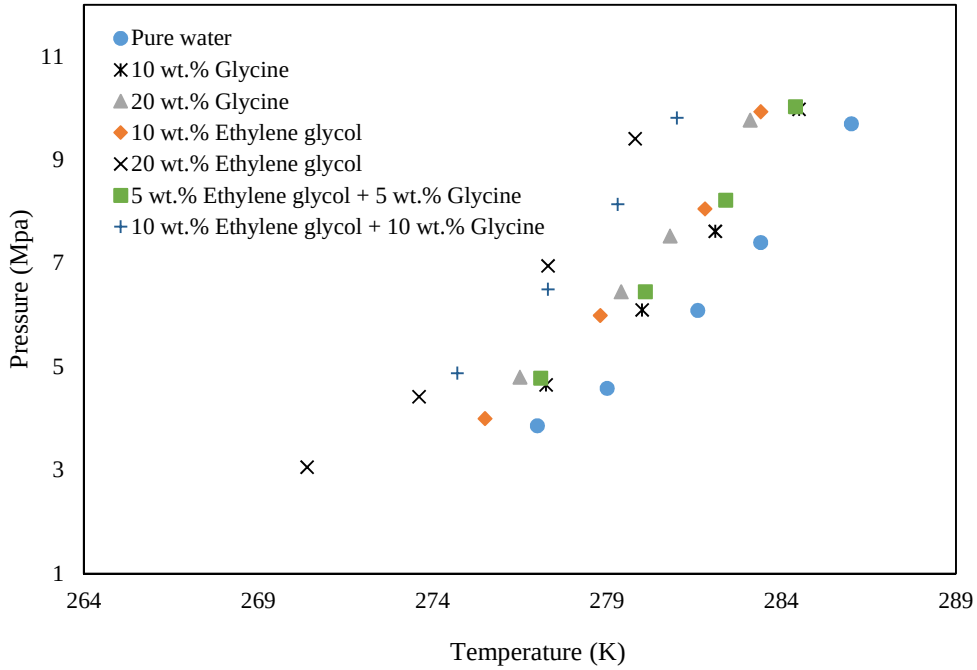


Figure 5. The inhibition impact of pure glycine and glycine + ethylene glycol on the HL_wVE data of CH_4 hydrates; Pure water and glycine data are taking from Bavoh et al., (2016b), glycol from Mohammadi and Richon, (2010), and glycine + ethylene glycol data from Long et al., (2018).

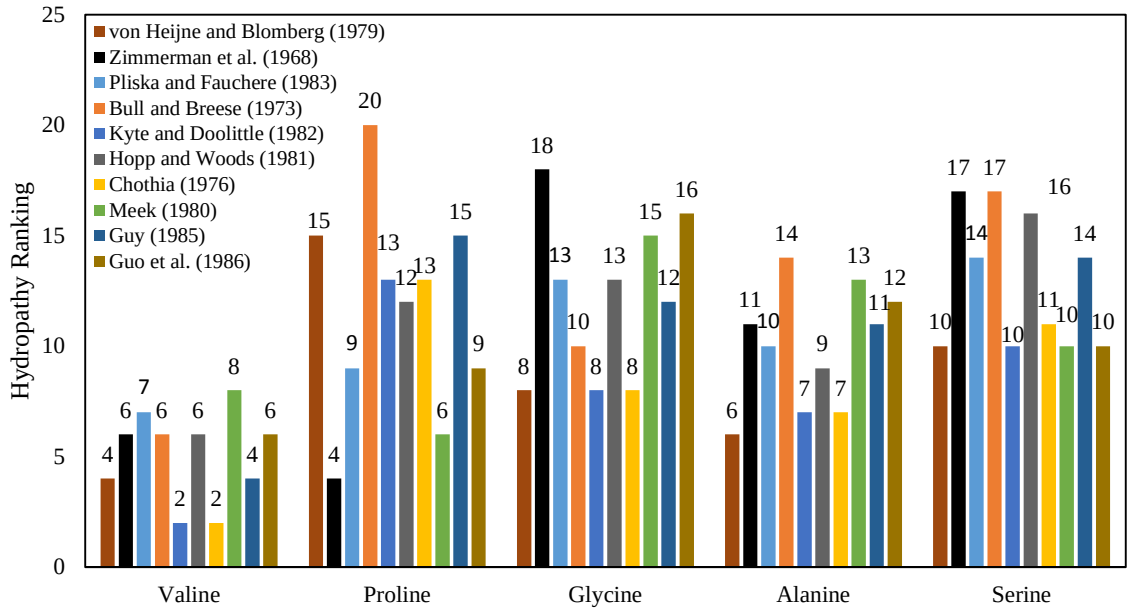
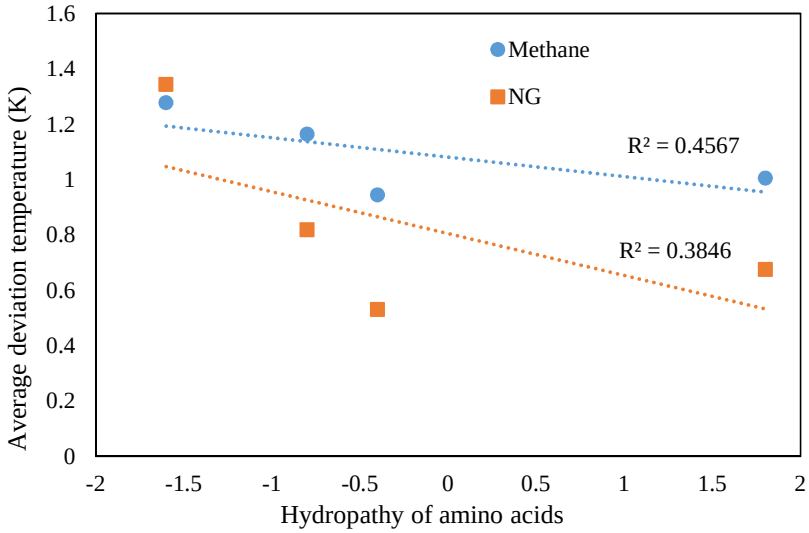
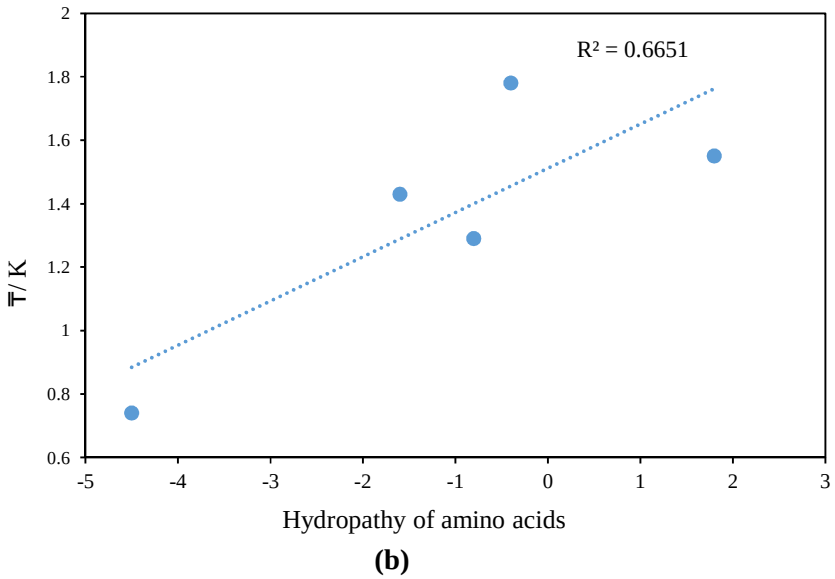


Figure 6. Hydropathy ranking of studied for gas hydrate inhibition. Data is taken from Wilce et al., (1995). The hydropathy of amino acids decreases with increasing ranking number.

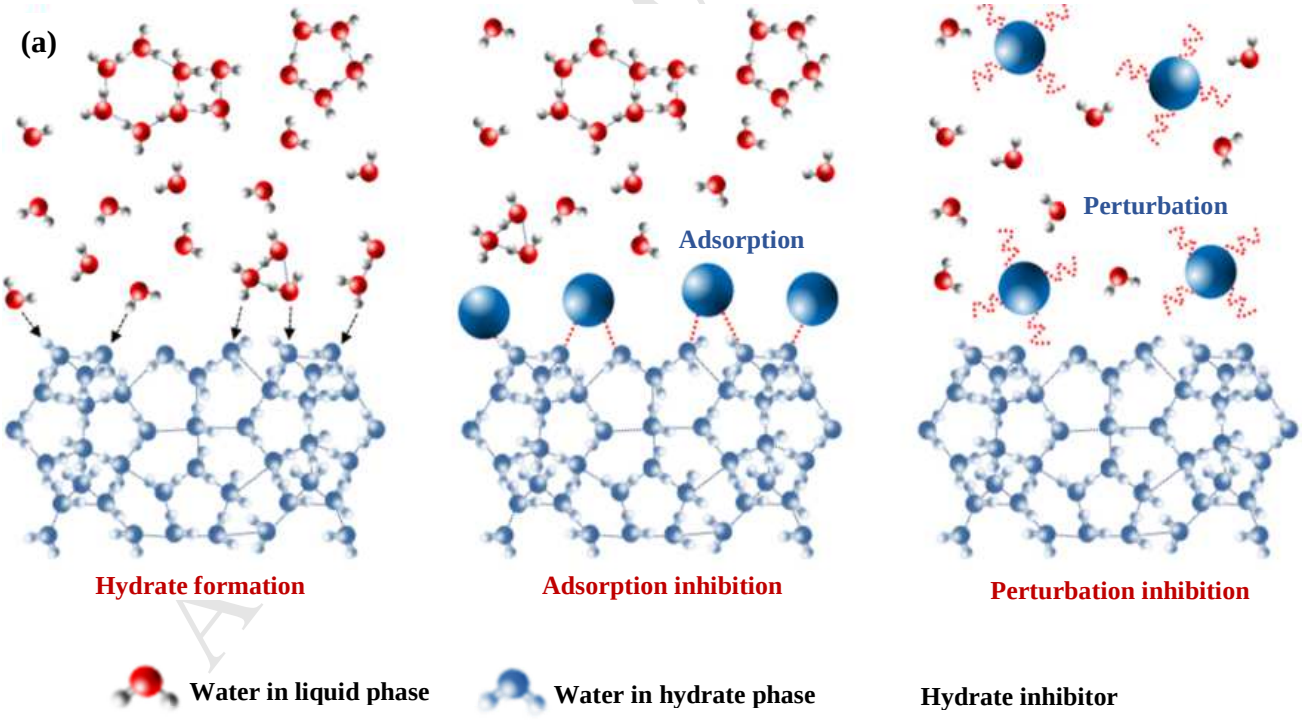


(a)



(b)

Figure 7. Regression between average depression temperature (Ŧ) and commonly used amino acid hydropathy scale proposed by Kyte and Doolittle, (1982); (a) data from Sa et al., (2016) and (b) data from Bavoh et al., (2016b).



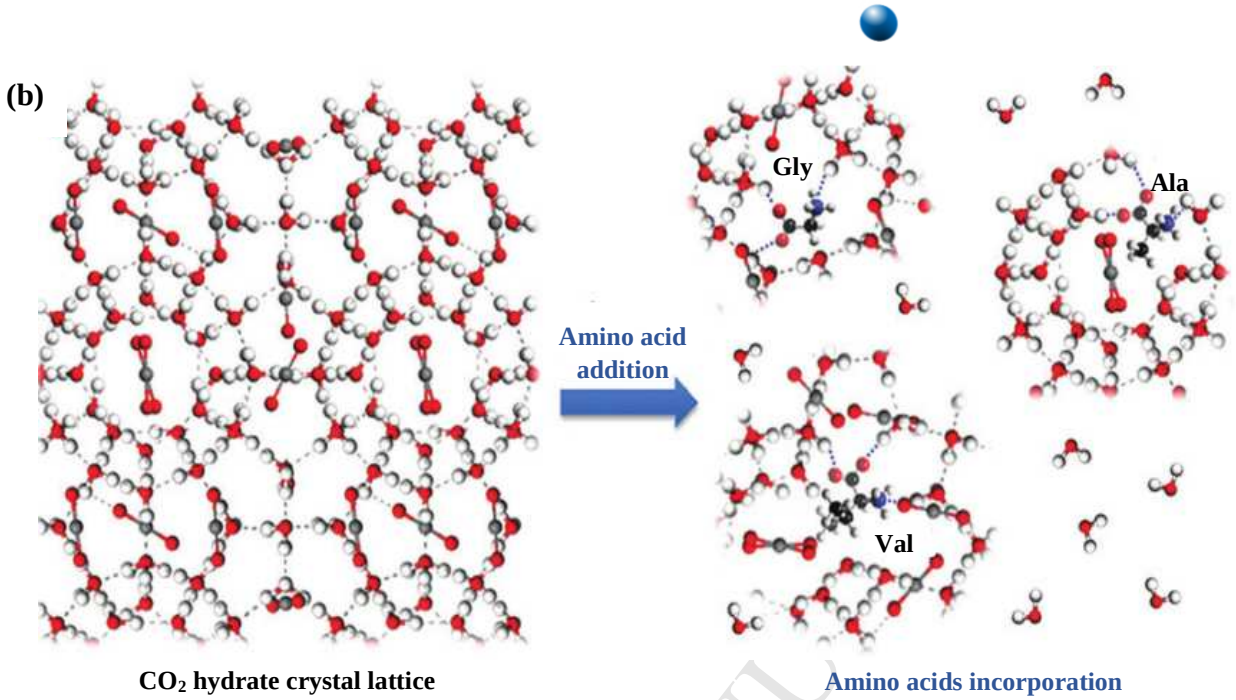
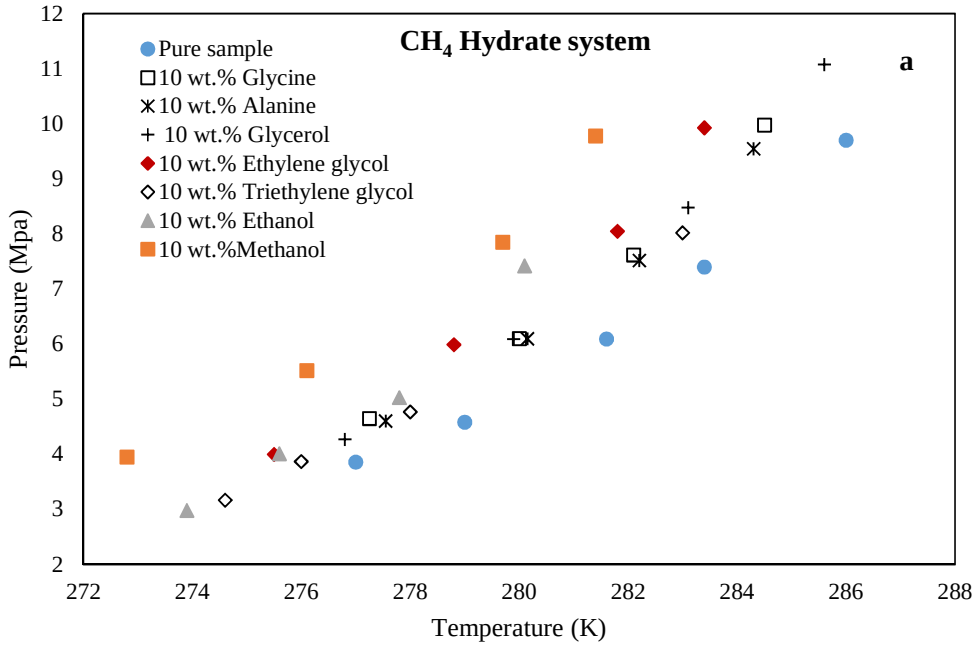


Figure 8. (a) amino acids gas hydrate growth inhibition mechanism by perturbation of the local water structure compared to adsorption inhibition mechanism (Sa et al., 2013); (b) amino acids lattice distortion and expansion inhibition mechanism through incorporation into gas hydrate crystal lattice (Sa et al., 2014). ©Nature Publishing Group. Reproduced by permission of Nature Publishing Group.



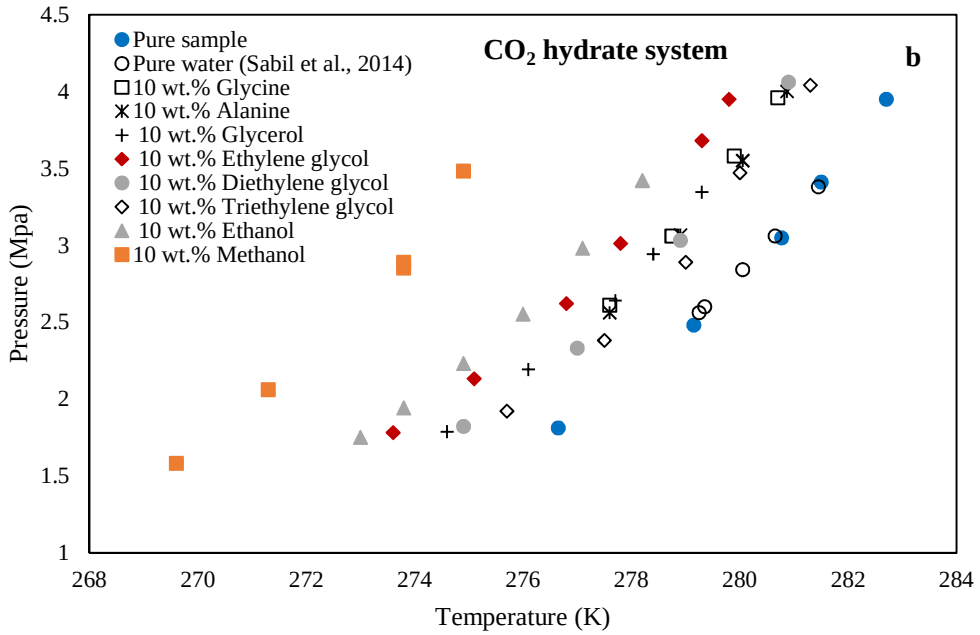


Figure 9. Comparison of the THI efficiency of amino acids and conventional additives for CH_4 and CO_2 hydrate system at 10 wt.%; the pure water data for CH_4 and CO_2 are taken from reference (Bavoh et al., 2017; Bavoh et al., 2016b; Nasir et al., 2014); (a) CH_4 hydrate system; (b) CO_2 hydrate system.

Highlights

1. The state of art on the use of natural amino acids in gas hydrate inhibition and CO_2 capture is presented.
2. Factors that affect amino acids inhibition/promotion effect on gas hydrate formation.
3. Gas hydrate systems, experimental details and data in the presence of amino acids are reported.

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